

Semiconducting π -Conjugated Systems in Field-Effect Transistors: A Material Odyssey of Organic Electronics

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1. INTRODUCTION

Since the discovery of highly conducting polyacetylene by Shirakawa, MacDiarmid, and Heeger¹ in 1977, π -conjugated systems have attracted much attention as futuristic materials for the development and production of the next generation of

electronics,² that is, organic electronics.³ Conceptually, organic electronics are quite different from conventional inorganic solid state electronics because the structural versatility of organic semiconductors allows for the incorporation of functionality by molecular design. This versatility leads to a new era in the design of electronic devices. To date, the great number of π -conjugated semiconducting materials that have either been discovered or synthesized generate an exciting library of π -conjugated systems for use in organic electronics.^{4–11} However, some key challenges for further advancement remain: the low mobility and stability of organic semiconductors, the lack of knowledge regarding structure–property relationships for understanding the fundamental chemical aspects behind the structural design, and realization of desired properties.

Organic field-effect transistors (OFETs) are a kind of device consisting of an organic semiconducting layer, a gate insulator layer, and three terminals (drain, source, and gate electrodes). OFETs are not only essential building blocks for the next generation of cheap and flexible organic circuits, but they also provide an important insight into the charge transport of π -conjugated systems. Therefore, they act as strong tools for the exploration of the structure–property relationships of π -conjugated systems, such as parameters of field-effect mobility (μ , the drift velocity of carriers under unit electric field), current on/off ratio (the ratio of the maximum on-state current to the minimum off-state current), and threshold voltage (the minimum gate voltage that is required to turn on the transistor).^{12–17} Since the discovery of OFETs in the 1980s,¹⁸ they have attracted much attention. Research on OFETs includes the discovery, design, and synthesis of π -conjugated systems for OFETs, device optimization, development of applications in radio frequency identification (RFID) tags, flexible displays,^{19,20} electronic papers,^{21,22} sensors,²³ and so forth. It is beyond the scope of this review to cover all aspects of π -conjugated systems; hence, our focus will be on the performance analysis of π -conjugated systems in OFETs. This should make it possible to extract information regarding the fundamental merit of semiconducting π -conjugated materials and capture what is needed for new materials and what is the synthesis orientation of new π -conjugated systems. In fact, for a new science with many practical applications, the field of organic electronics is progressing extremely rapidly. For example, using “organic field effect transistor” or “organic field effect transistors” as the query keywords to search the Web of Science citation database, it is possible to show the distribution of papers over recent years as shown in Figure 1A. It is very clear

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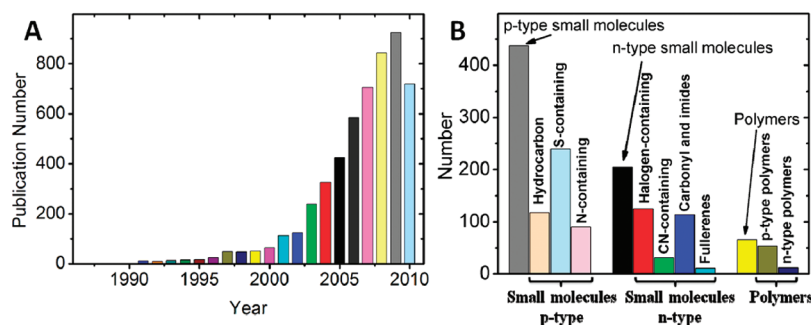


Figure 1. (A) Distribution of published papers by year using “organic field effect transistor” or “organic field effect transistors” as query keywords for Web of Science citation database. (B) Distribution of reviewed π -conjugated systems in this review.

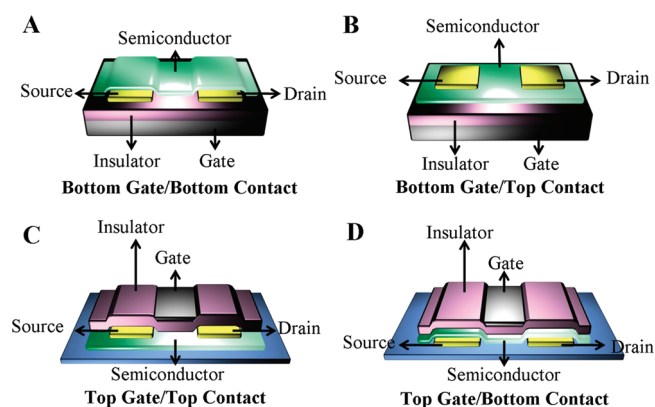


Figure 2. Four types of OFETs. (A) Bottom gate/bottom contact, (B) bottom gate/top contact, (C) top gate/top contact, and (D) top gate/bottom contact.

that the number of papers concerning OFETs has increased exponentially since 2000. In particular, since 2008 over 2000 papers have been published. Therefore, a review in this field is not only timely but also imperative. It is hoped that a general overview covering the most important progress in this field will facilitate readers and help to prevent them being submerged by the flood of references. Here, this comprehensive review of π -conjugated systems will cover over 700 π -conjugated systems, including 438 p-type small molecules, 205 n-type small molecules, and 66 polymer semiconductors (Figure 1B). It is hoped that the analysis of these π -conjugated systems will contribute to a better understanding of structure–property relationships of such compounds, in such a way that the design of new materials with a view to achieving desired performance in devices and circuits will be facilitated.

2. FACTORS INFLUENCING DEVICE PERFORMANCE

There is a wealth of literature available on the fundamental physics of OFETs.^{9,24,25} Principally, an OFET can be regarded as a capacitor, wherein the semiconductor layer and the gate electrode act as electrodes to sandwich the gate insulator. When gate electrode is applied, voltage charges injected from the source electrode will be attracted to the interface of the gate insulator and organic semiconductor. Then, if a drain-source voltage is applied, a current between the source and drain electrodes will be generated, which in turn can be tuned by the gate voltage. According to the adopted device configuration, OFETs can be divided into four different types as shown in Figure 2: the bottom

gate bottom contact (A), the bottom gate top contact (B), the top gate top contact (C) and the top gate bottom contact (D).

Undoubtedly, the device configuration plays a key role in the device performance. For example, it was found that devices of the type B and D always give better performances than that of devices A and C. This was attributed to the improved contact between the organic semiconductor and the electrodes.²⁶ It is certain that in addition to the device configuration, other factors, such as the semiconductor layer (e.g., the chemical structure and intermolecular interaction of organic semiconductor, the morphology and molecular arrangement in the active layer), the materials used for the electrodes and the gate insulator, the interface and energy alignments between the organic semiconductor and the gate insulator or between the organic semiconductor and the electrodes etc., all play crucial roles in the ultimate performance of OFETs.

2.1. Factors Influencing by Semiconducting π -Conjugated Systems

There is no doubt that the semiconducting π -conjugated system incorporated into OFETs is one of the most important factors determining the ultimate performance of the device. Principally, the mobility of the organic semiconductor should be as high as possible so that efficient charge transport from one molecule to another is attainable. This in turn is intimately related to the electron cloud on the molecule and the electron cloud splitting with its neighbor molecules. Two parameters, the transfer integral and the reorganization energy, are both believed to be highly important for the mobility of organic semiconductors. The transfer integral means the splitting of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). This in turn depends to a large extent on the π -overlap between neighbouring molecules.²⁷ The reorganization energy is the energy loss when a charge carrier passes through a molecule and is dependent on the conjugation length, degree, and packing of the organic molecules.^{28–31} Usually, the larger the transfer integral and the smaller the reorganization energy, the higher the mobility will be.^{30,32}

The transfer integral and reorganization energy are both extremely dependent on the packing (arrangement) of the organic molecules.²⁷ Therefore, the packing mode of the organic semiconductors becomes very important for the analysis of the charge transport between molecules. There are four different kinds of packing motifs as shown in Figure 3:^{33–35} (1) herringbone packing (face-to-edge) without π – π overlap (face-to-face) between adjacent molecules; (2) herringbone packing with π – π overlap between adjacent molecules, also called slipped π –stacking

in some literature reports;³⁶ (3) lamellar packing, one-dimension (1-D) π -stacking, and (4) lamellar packing, two-dimension (2-D) π -stacking. Of the four kinds of packing motifs, that of lamellar packing (2-D π -stacking) is believed to be the most efficient for charge transport³⁴ because it can increase the transfer integrals to the maximum and transport the charge carriers through an almost straight line (namely, the shortest route). Much research has focused on molecular design and crystal engineering in order to obtain 2-D lamellar packing. Some examples are substitution at the peri-positions of acenes (sections 3.1.1.3 and 3.1.2.1), introducing polarity (section 3.1.1.1), increasing the C/H ratio (section 3.1.1.1) or adding heteroatoms to generate hydrogen bonds, halogen-halogen interactions or chalcogen-chalcogen interactions (sections 3.1.2 and 3.1.3). The intrinsic properties of organic semiconductors can be tracked by using their single crystals because organic crystals provide highly ordered structures, minimized traps and are free from grain boundaries. Certainly, one challenge needing to be recognized is how to fabricate devices based on their crystals because organic crystals are not only usually very fragile but also very small.^{37,38}

2.2. Factors Influencing by Device Physics

Both the morphology and molecular arrangement in organic semiconducting layers play significant roles in the performance of

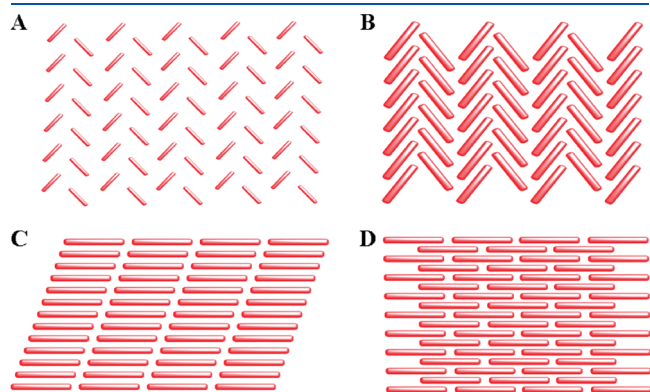


Figure 3. Molecular packing motifs in crystals. (A) Herringbone packing (face-to-edge) without π - π overlap (face-to-face) between adjacent molecules (example: pentacene); (B) herringbone packing with π - π overlap between adjacent molecules (example: rubrene); (C) lamellar motif, 1-D π -stacking (example: hexyl substituted naphthalene diimide); (D) lamellar motif, 2-D π -stacking (example: TIPS-PEN). Adapted with permission from refs 39 and 35. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA and Copyright 2010 Royal Society Chemistry.

OFETs. In order to achieve a more efficient charge transport, ideally the organic molecules should pack along the current direction in the conducting channel. This in fact is the reason why high performance organic field-effect transistors usually adopt an edge-on orientation. A possible mechanism scenario using a polymer as the example is shown in Figure 4. There is no doubt that, due to their perfect molecular arrangements, free of grain boundaries, and minimized charge traps, single crystal transistors should display higher performances than those of thin films. Hence, well-ordered, continuous films, especially crystalline films, are being seriously investigated for high performance OFET applications.

The dielectric constant of the gate insulator and the interface effect between the gate insulator and the organic semiconductor also take on important roles in the performance of OFETs. Gate insulators with high dielectric constants (high k)⁴³ are preferable for use in organic devices because using a high k insulator makes it possible to scale down the device dimensions, lower the driving voltage, and increase the integrated degree of the organic circuit. The interface between the gate insulator and the organic semiconductor will affect not only the morphology and molecular arrangement of the semiconducting layer but also the adhesion of the organic semiconductor on the gate insulator, that is, to create an intimate interface contact. Among the possible candidates for gate insulators, polymer insulators are highly promising because they exhibit not only ideal flexibility for flexible electronics but also promote intimate contact with the organic semiconductors.⁴²

Without doubt the materials used for the electrodes are critical for the fabrication of high performance devices. Ideally the materials should have high conductivity, high stability, good adhesion ability with the organic semiconductors, and finally an optimized energy alignment with the organic semiconductors. The importance of the latter for charge injection and transport will be discussed in section 3.2. Electrode materials can be manufactured from a variety of materials including metals (e.g., Au, Ag), heavily doped silicon, metallic conductive oxides (e.g., indium tin oxide), and conductive organic molecules such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), tetrathiafulvalene-tetracyanoquinodimethane complex and graphene, etc. Conductive organic molecules are especially intriguing for the fabrication of high performance devices due to their unique ability to form intimate contacts with organic semiconductors to produce high quality interfaces.⁴⁴

It is generally accepted that the purity of organic semiconductors, the thickness of the dielectric and semiconducting layers, the channel length,⁴⁵ and the testing environment (the temperature, vacuum conditions etc.) all influence the device properties.

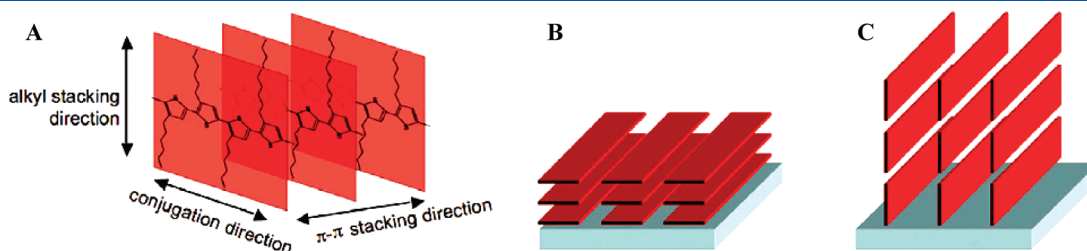
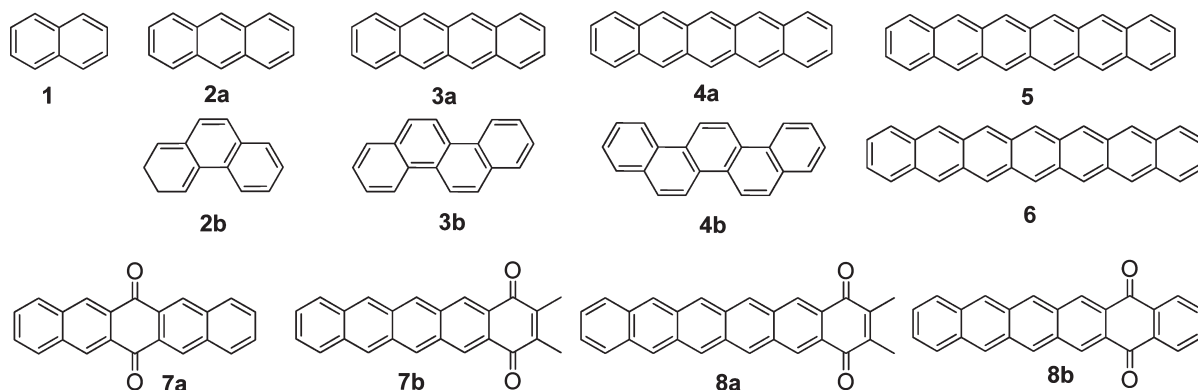


Figure 4. (A) Possible charge transport mechanisms in crystalline polymer films (using P3HT for illustration): Intrachain transport, along the π -conjugation direction (example: TA-PPE (152b)⁴⁰) and interchain transport, along the π -stacking direction (example: P3HT (144a)⁴¹) or alkyl stacking direction. (B) Face-on and (C) edge-on orientation of the polymer molecules on the substrates. Reprinted with permission from ref 42. Copyright 2007 Elsevier B.V.

Chart 1. Acenes and Acene-dione



The relevant physics for the devices of interest will be further clarified in section 6.2.

3. SMALL MOLECULE SEMICONDUCTORS

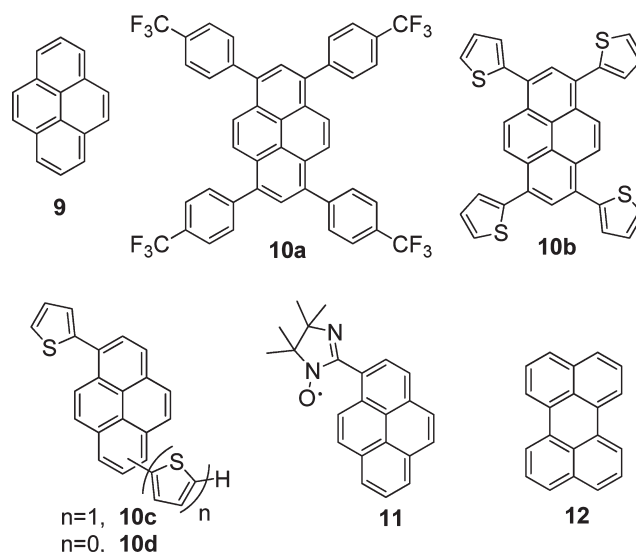
Small molecule semiconductors have been widely studied because they are easy to purify and easily form crystalline films for the fabrication of the desired high performance devices. Indeed, up until now, the π -conjugated systems that are reported to have the highest mobility are small molecules such as pentacene, rubrene, C8-BTBT, and titanyl phthalocyanine (TiOPc).

3.1. p-Type Small Molecule Semiconductors

3.1.1. Aromatic Hydrocarbons and Derivatives. Typical acenes and fused arenes of aromatic hydrocarbons as seen in Charts 1–3^{6,7} show ideal transistor behaviors when employed in OFETs. Their π -conjugated systems are similar to that of single layer of graphite, that is, graphene (to date, the aromatic compound with the highest mobility and which recently won its discoverers the 2010 Noble Prize in physics). Here, we will discuss the aromatic hydrocarbons according to their conjugated dimensions going from naphthalene (1) and anthracene (2a) to graphene (13).

3.1.1.1. Acenes. Naphthalene (1) and anthracene (2a) can be considered as less extended acenes. Single crystals of naphthalene have been studied by using the time-of-flight (TOF)⁴⁶ method, but few reports have actually addressed the use of naphthalene in OFETs. Anthracene has also been examined in OFETs and its single crystal devices exhibited mobility at $0.02 \text{ cm}^2/(\text{V}\cdot\text{s})$ at low temperature.⁴⁷ It is believed that the performance of anthracene OFETs could be further optimized since the hole mobility of anthracene could approach $3 \text{ cm}^2/(\text{V}\cdot\text{s})$ according to the results of room temperature TOF.^{48,49} Normally, with the expansion of the π -conjugated dimension, the intermolecular overlap of the electron cloud is increased, and this results in a larger transfer integral and lower reorganization energy.²⁸ Gundlach et al.⁵⁰ found that thin film field-effect transistors of tetracene (3a) showed a mobility of $0.1 \text{ cm}^2/(\text{V}\cdot\text{s})$ with a current on/off ratio over 10^6 on octadecyltrichlorosilane (ODTS)-modified SiO_2 substrates. Its single crystal transistors⁵¹ provided a mobility of $2.4 \text{ cm}^2/(\text{V}\cdot\text{s})$ by using poly(dimethylsiloxane) (PDMS) as the dielectric layer. Thin film transistors⁵² of pentacene (4a) demonstrated mobilities of up to $1.5 \text{ cm}^2/(\text{V}\cdot\text{s})$ with an on/off ratio over 10^8 , threshold voltage at about 0 V, and a subthreshold slope less than 1.6 V/decade. In addition, Kelly et al. even found that the

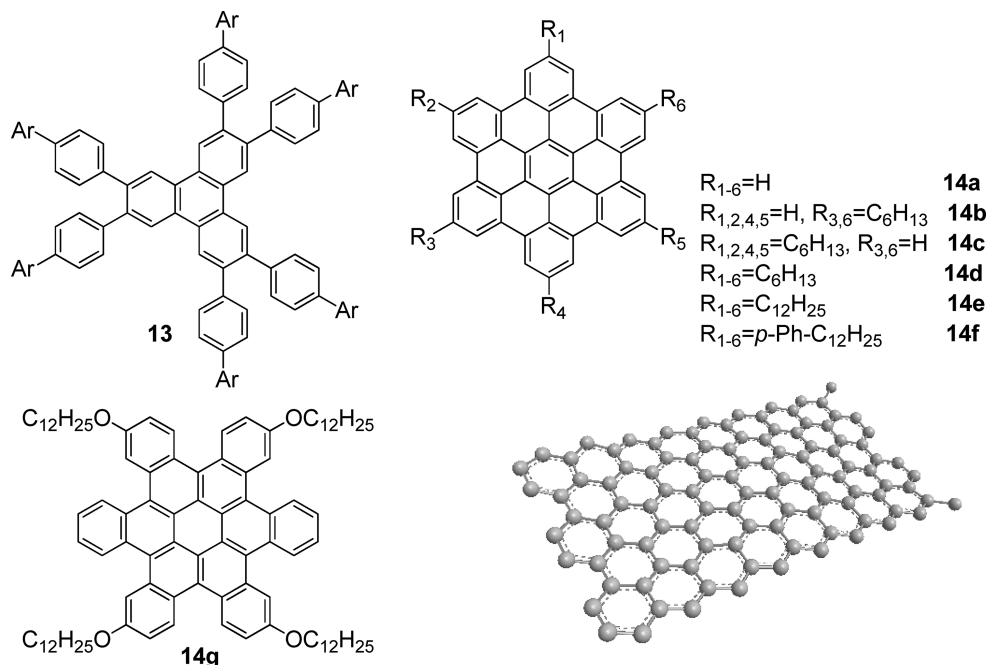
Chart 2. Pyrene and Perylene



mobility of pentacene could approach $5.0 \text{ cm}^2/(\text{V}\cdot\text{s})$ with an on/off ratio over 10^6 when polycrystalline films of pentacene were used in OFETs.⁵³ Clearly, the field-effect mobility is increasing on going from anthracene to pentacene with the extension of the π -conjugated systems. This is attributed to the associated benefits of intermolecular π -orbital overlap and the fact that charge transport is facilitated (for larger transfer integral and lower reorganization energy).

One disadvantage of using higher acenes is not only their high sensitivity to light because of their narrow energy gaps (from anthracene,⁵⁴ tetracene,⁵⁵ to pentacene:⁵⁶ 4.0, 2.6, 1.8 eV) leading to easy molecular excitation by light but also their high HOMO energy levels (from anthracene,⁵⁴ tetracene,⁵⁵ to pentacene:⁵⁶ -5.7 , -5.2 , -5.0 eV) which results in high oxidation sensitivity to oxygen. For example, pentacene easily forms dimers and trimers in ambient conditions or can be oxidized into 6,13-pentacenequinone (7a, PQ). Moreover, the solubility of pentacene is also very poor in common organic solvents.⁴⁹ The result is that the purification of pentacene is highly challenging (ultrapure pentacene is almost impossible to obtain due to the existence of PQ. For example, even after repeated sublimation⁵⁷ the PQ concentration was still 0.028%. However, when utilizing this PQ

Chart 3. Coronene and Other Fused Arenes



as the gate dielectric to fabricate single crystal field-effect transistors of pentacene, Palstra et al.⁵⁸ achieved a mobility as high as $15\text{--}40\text{ cm}^2/(\text{V}\cdot\text{s})$ with a current on/off ratio of up to 10^6 . This was attributed to the fact that PQ has a structure similar to pentacene and this provides an intimate contact between the semiconductor and the dielectric layer. With a further increase in the number of benzene rings for extension of the π -conjugated systems, the stability and solubility of the larger acenes become even poorer so that OFETs based on hexacene (**5**)⁵⁹ and heptacene (**6**)⁶⁰ have never been addressed.

Picene (**4b**)⁶¹ is an isomeric compound of pentacene but shows higher stability because its energy band gap is larger ($E_g = 3.3\text{ eV}$) and its ionization potential is higher (IP = 5.5 eV) than those of pentacene ($E_g = 1.8\text{ eV}$, IP = 5.0 eV). The OFET performance of picene exhibited typical p-channel characteristics with a mobility of $1.1\text{ cm}^2/(\text{V}\cdot\text{s})$ and an on/off ratio of 10^5 under atmospheric conditions. The mobility was found to approach $3.2\text{ cm}^2/(\text{V}\cdot\text{s})$ if the device was exposed to O_2 for oxygen doping.⁶²

In fact, there is a balance between the π - π interaction and the electrostatic repulsion in acenes, and this balance usually results in a herringbone angle between neighboring molecules. If polar groups are introduced into the molecular structure, a new balance can be achieved with the result that the packing motifs may even shift, for example, from herringbone to lamellar stacking.³⁴ For example, the acene-diones (**7b** and **8a–b**)⁶³ adopt lamellar stacking instead of herringbone packing in solid films. This indicates that the introduction of polar groups is an efficient way to change the molecular packing and obtain π - π stacking acenes (Figure 5). As a result acene derivatives have been widely studied and hence will be further discussed in section 3.1.1.3.

3.1.1.2. Pyrene, Perylene, Coronene, and Other Fused Arenes. It is useful to compare the linear acenes such as tetracene and pentacene which have the herringbone packing motif, with pyrene and perylene which, although they have the same number of benzene rings as that of tetracene and pentacene, exhibit π - π

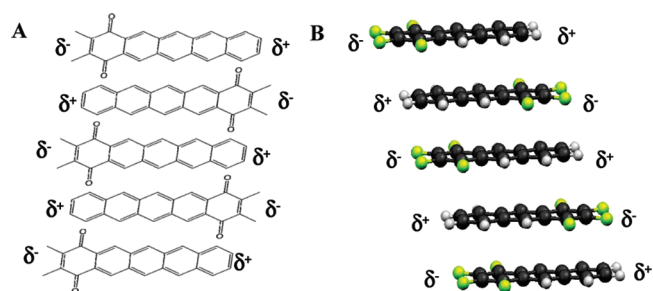


Figure 5. Lamellar acene structures produced by introducing polar groups into the molecular structures to balance the electrostatic repulsion, (A) **7b**, (B) 1,2,3,4-tetrafluoroanthracene (RefCode MIKGOD from CSD).⁶⁴

stacking motif in crystals. Although it has been reported that highly purified pyrene (**9**)^{65,66} showed a hole mobility of $1.2\text{ cm}^2/(\text{V}\cdot\text{s})$ and an electron mobility of $3\text{ cm}^2/(\text{V}\cdot\text{s})$ at room temperature, judging from the transient photocurrent of the pyrene crystal and calculating from the overlap integrals between two molecules, however, the pyrene derivatives (**10a–d**)^{67,68} when used in OFETs exhibited rather low mobilities. This is probably due to the nonplanar structure of the compounds concerned. Liu and Zhang et al. reported the use of pyrene organic radicals in OFETs. Here 1-imino nitroxide pyrene (**11**) was used as the active semiconducting layer,⁶⁹ and they achieved a mobility of up to $0.1\text{ cm}^2/(\text{V}\cdot\text{s})$ with an on/off ratio at 5×10^4 . This achievement opened the door for the application of organic radicals in OFETs. Studies on perylene (**12**) suggested that this compound gave field-effect mobility at around $0.12\text{ cm}^2/(\text{V}\cdot\text{s})$, which was of the same order as in the TOF results ($0.15\text{--}0.3\text{ cm}^2/(\text{V}\cdot\text{s})$)^{70–72} for the same compound.

Triphenylenes and coronenes are extensively studied as organic liquid crystal materials because of their unique tendency to

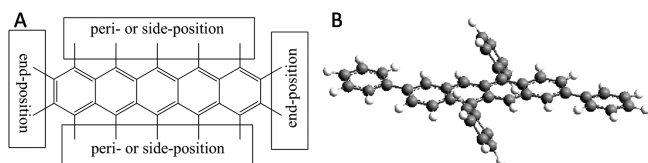


Figure 6. (A) Schematic diagram of substituents in the peri- (or side-) and end-positions; (B) simulated structure of acene derivatives with peri- and end-position aryl substituents: peri-phenyl substituents display a twisting angle with the acene core. End-phenyl substituents extend planar core structure.

aggregate into one- or two-dimensional (1D or 2D) columnar arrays.⁷³ However, triphenylenes and their derivatives (see **13** as an example)^{74,75} are rarely studied with respect to OFET applications and in fact showed rather low performance. Coronenes such as hexabenzocoronene (HBC, **14a**)⁷⁶ and their derivatives **14b–f**^{77–79} and **14g**⁸⁰ exhibit disk-shaped structures, which are efficient for extending their π -systems to form 2D columnar stacking structures. Indeed, it was found that the dihexyl derivative (2H-HBC, **14b**) and tetrahexyl derivative (4H-HBC, **14c**) both realized 2D columnar stacking structures and together with the hexahexyl derivative (6H-HBC, **14d**) all showed one-dimensional conducting pathways. By applying a high magnetic field, a high mesoscopic order⁷⁸ was obtained in thin films of HBC derivatives (**14f**) with a discotic liquid crystal phase. The aligned films provided mobility with a 10-fold enhancement and ultra-high anisotropy up to 75 times over the corresponding unaligned films. Self-assembly characteristics and field-effect properties of **14g**⁸⁰ were also examined. Spin-cast films showed mobility at $0.02 \text{ cm}^2/(\text{V}\cdot\text{s})$ with a current on/off ratio of about 10^6 . Where graphene (**15**) is concerned, it could in fact be regarded as the “unlimited” extension of the conjugated dimension of such aromatic hydrocarbons and hence exhibited excellent field-effect properties^{81,82} in particular high mobility.

On going from acenes to fused ring aromatics, it is obvious that (i) the extension of π -conjugated system increases the transfer integrals and lowers the reorganization energies, (ii) the increased C/H ratio leads to π – π stacking which is advantageous for high mobility. Certainly, the solubility, stability,⁸³ planar conjugation,⁸⁰ and molecular packing all need further consideration in order to extend the practical applications of aromatic hydrocarbons and their derivatives.

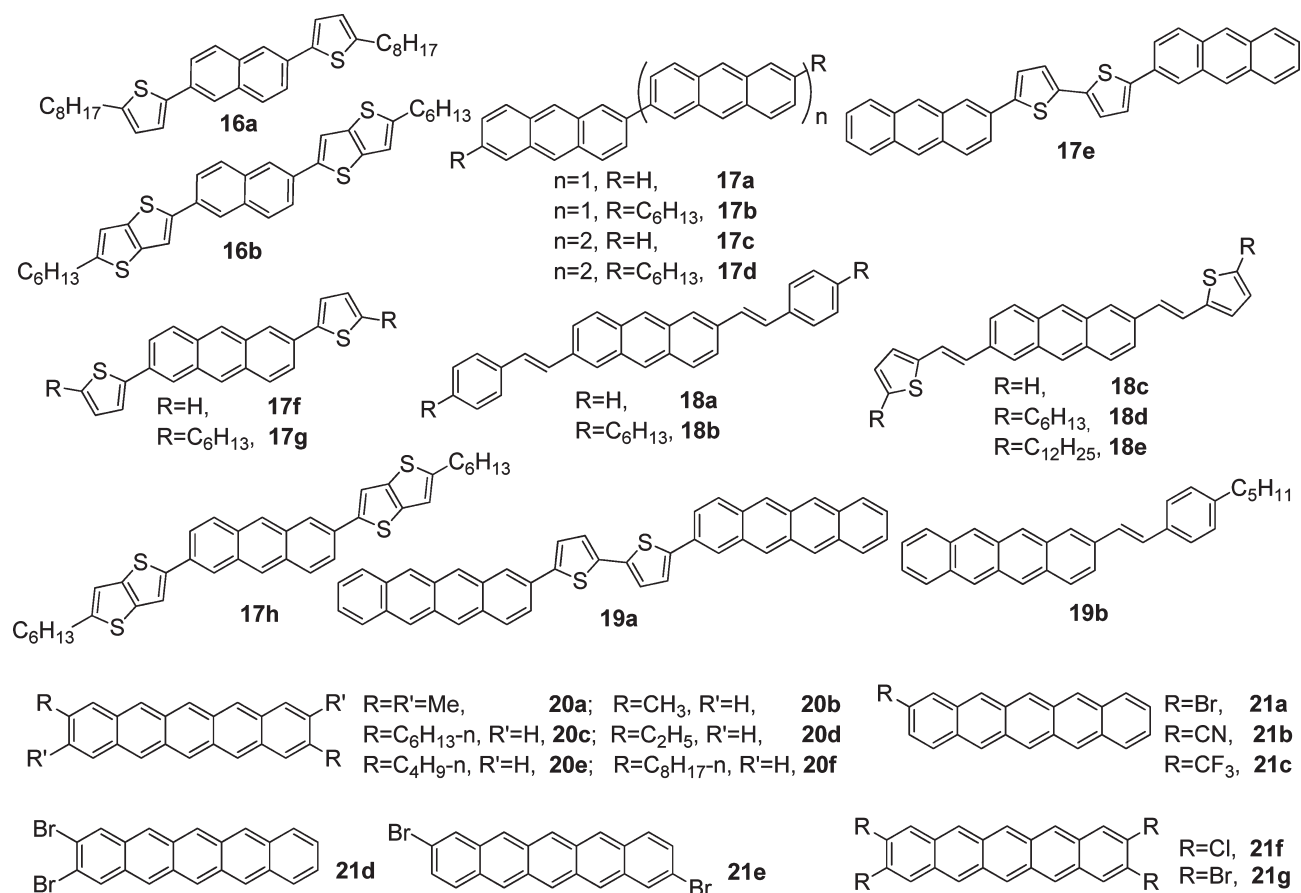
3.1.1.3. Oligoacenes. Studies on oligoacenes are mostly focused on anthracene, tetracene, pentacene and their derivatives. Depending on the position of the substituents, oligoacenes can be divided into two kinds: (i) substituents on the peri- (or side-) and (ii) end-positions (Figure 6). For smaller acenes, substituents usually are conjugated units to extend their π -conjugation, while for larger acenes substituents are usually aimed to improve their solubility, stability, and molecular packing.

Oligomers substituted in the end-positions are expected to give rise to an extended π -conjugation system and high planarity. This is because their linearity is capable of eliminating any steric hindrance (as shown in Figure 6B).⁴⁹ Those oligomers that combine a naphthalene core with thiophene (**16a**)⁸⁴ or thienothiophene (**16b**)⁸⁵ exhibited mobilities at 0.14 and $0.084 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively. However, studies of naphthalene-based materials are still rare. In contrast, oligomers based on anthracene substituted in the 2- and 6-positions have been intensively studied. This is because the optimum conjugated

length of these compounds provides (i) higher mobility than that of naphthalene and (ii) higher stability than either tetracene or pentacene. Suzuki et al. synthesized a series of oligo(2,6-anthrylenes) (**17a–d**)⁴⁹ linked by single bonds. On going from **17a** to **17d**, the mobilities of the films were found to be about 0.01, 0.13, 0.07, $0.18 \text{ cm}^2/(\text{V}\cdot\text{s})$. These results going from **17a** to **17b** and **17c** to **17d** suggest an increased mobility with the addition of alkyl groups. After careful treatment of the insulator surface with octyltrichlorosilane (OTS),⁸⁶ the mobility of **17a** reached $1.0 \text{ cm}^2/(\text{V}\cdot\text{s})$. Derivatives^{87,88} of anthracenes substituted by thienyl (**17f**) and alkylthienyl (**17g**) in the 2- and 6-positions showed a similar mobility tendency on the addition of alkyl groups. The mobility of **17g** was about $0.5 \text{ cm}^2/(\text{V}\cdot\text{s})$, which was nearly 1 order of magnitude higher than **17f** ($0.06 \text{ cm}^2/(\text{V}\cdot\text{s})$). When the oligomer **17e**⁸⁹ was combined with anthracene and 2,2'-bithiophene, the resulting molecule also showed a mobility of $0.1 \text{ cm}^2/(\text{V}\cdot\text{s})$. The corresponding thienothiophene-based co-oligomer **17h**⁸⁵ exhibited a mobility of $0.14 \text{ cm}^2/(\text{V}\cdot\text{s})$. A series of anthracene derivatives linked by double bonds was designed by Meng and co-workers who found that the compounds exhibited extremely high OFET performance. For instance, **18a** (DPVAnt)⁵⁶ and **18b** (DPPVAnt)⁹⁰ films showed mobilities as high as $1.3 \text{ cm}^2/(\text{V}\cdot\text{s})$ (its single crystal exhibited mobility⁹¹ of up to $4.3 \text{ cm}^2/(\text{V}\cdot\text{s})$ along the *a*-axis) and $1.28 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively. On the other hand, under similar experiment conditions, highly purified pentacene showed a maximum mobility at $1.05 \text{ cm}^2/(\text{V}\cdot\text{s})$. In addition, **18b** was found to be more stable than pentacene. After being stored at an ambient atmosphere for 1 month, the pentacene-based devices exhibited a mobility of $0.03 \text{ cm}^2/(\text{V}\cdot\text{s})$ with an on/off ratio lower than 10^2 . In contrast, after storage under ambient conditions for over 20 months, the mobility of **18b** was maintained at $0.95 \text{ cm}^2/(\text{V}\cdot\text{s})$ with an on/off ratio over 10^6 . Similarly, the derivatives (**18c–e**),⁹² in which phenyl substitutions were replaced by thienyl, also exhibited high field-effect performance. **18c** showed a field-effect mobility of up to $0.4 \text{ cm}^2/(\text{V}\cdot\text{s})$ about 7 times larger than DTAnt (**17f**) without vinyl groups under similar conditions. This strongly supports the importance of double bonds for extension of the π -system and improving the mobility. However, hexyl (**18d**) and dodecyl (**18e**)⁹³-substituted derivatives showed mobilities at 0.15 and $0.05 \text{ cm}^2/(\text{V}\cdot\text{s})$. The fact that these were much lower than that of **18c** was attributed to their less-ordered structures. Oligomers based on tetracene in the end-positions have been rarely reported. This is probably due to the inactivity of these end-positions and their somewhat unobvious effect on packing motifs. This will be further illustrated in the section on pentacene derivatives. The tetracene derivatives **19a**⁸⁹ and **19b**⁹⁴ showed mobilities at 0.5 and $0.2 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively.

Studies on pentacene derivatives are usually focused on the improvement of solubility and stability. However, the alkyl substituents at the end-positions showed unobvious improvement for stability. For example, the thermal stability of 2,3,9,10-tetramethyl-pentacene (Me₄PENT, **20a**)⁹⁵ was much better than that of pentacene, but it is more susceptible to oxidation than pentacene due to its higher HOMO energy level (about 0.2 eV higher than pentacene). OFETs based on Me₄PENT exhibited a mobility of $0.31 \text{ cm}^2/(\text{V}\cdot\text{s})$ with an on/off ratio at 10^3 . Derivatives of dialkyl substituted pentacene were also studied. Kelley's group tested the charge transport properties of 2,9-dimethylpentacene (**20b**)⁹⁶ and found mobility was as high as $2.5 \text{ cm}^2/(\text{V}\cdot\text{s})$ with an on/off ratio up to 10^6 . On the other hand, 2,9-dihexylpentacene

Chart 4. Oligomers Based on Linear Acenes Substituted at the End-Positions



(20c) showed a much lower mobility of about $0.251 \text{ cm}^2/(\text{V}\cdot\text{s})$. Other 2,9-dialkylpentacene derivatives (20d–f)⁹⁷ showed even poorer field-effect performance than 2,9-dihexylpentacene, and the mobility decreased with the increase in alkyl-chain length. In order to improve the stability, electron-withdrawing groups (such as halogen, cyano, and trifluoromethyl moieties)^{98,99} can be introduced into pentacene to lower its HOMO energy levels and the reactivity of the pentacene core. 21d exhibited the highest performance with a mobility of $0.22 \text{ cm}^2/(\text{V}\cdot\text{s})$ and an on/off ratio of about 10^5 . No significant degradation was observed in its devices after exposure to air and under light for 80 days.

Studies have shown that acenes substituted at the peri-positions (or side positions) could prevent the $C-H\cdots\pi$ intermolecular interactions (edge-to-face) and lead to $\pi-\pi$ stacking (face-to-face, or even turn into a lamellar structure; see Figure 7 for an example). This in turn facilitates charge transport^{6,100,101} and improves device mobility. Moreover, the peri-positions (for instance, the 6- and 13-positions of pentacene or the 9- and 10-positions of anthracene) constitute the active centers of acenes which are easily functionalized. As a result, derivatives of acenes substituted in the peri-positions have been studied widely in order to obtain a better packing motif in their crystals with a view to enhancing the solution processability as well as increasing acene stability.

There has been a wealth of studies of anthracene derivatives substituted at the 9- and 10-positions. TOF results suggest that single crystals of 9,10-diphenylanthracene (DPA, 22)¹⁰² exhibit a hole mobility of $3.7 \text{ cm}^2/(\text{V}\cdot\text{s})$ and an electron mobility of

$13 \text{ cm}^2/(\text{V}\cdot\text{s})$. The high performance of DPA was attributed to the large $\pi-\pi$ overlap (face-to-face) between its neighboring molecules. This indicates that substitutions in the peri-positions of acenes are in fact favorable to $\pi-\pi$ stacking. However, it should be noted that DPA is actually a nonplanar molecule. The dihedral angle^{102,103} between the planes of substitution (benzene ring) and core (anthracene) is about 67° (the derivatives substituted in the 2- and 6-positions, as mentioned above, show an almost planar structure⁸⁸), so that crystalline films of DPA were difficult to obtain, and device mobility¹⁰⁴ of the individual nanoribbon was only $0.16 \text{ cm}^2/(\text{V}\cdot\text{s})$. The corresponding dihedral angles^{105,106} of other derivatives with substituents in the 9- and 10-positions were also about 70° . This presents a real challenge for their application in thin film transistors. Faced with such a challenge, carbon-carbon triple bonds^{107–110} were introduced into this kind of molecule. As a result, nearly planar anthracene derivatives (23a–c, 23e) were obtained, and strong $\pi-\pi$ intermolecular interactions were found in these materials. Taking BPEA (23a) as an example, the π -overlap (face-to-face) dimension between neighboring molecules was about one benzene ring and the distance of $\pi-\pi$ stacking was about 3.4 \AA . The oligo(9,10-anthrylenes) (23d,¹⁰⁸ 23e,¹⁰⁹ 23f¹¹⁰) linked by triple bonds showed a similar $\pi-\pi$ overlap to that of the oligo(2,6-anthrylenes)⁴⁵ in crystals. Anthracene derivatives with substituents at the 1,4,5- and 8-positions were rarely studied for OFET applications because these derivatives could not extend their π -conjugated systems as efficiently as in the case of 2,6-substituents or 9,10-substituents. Miao et al. synthesized some anthracene derivatives (24a, 24b)¹¹¹

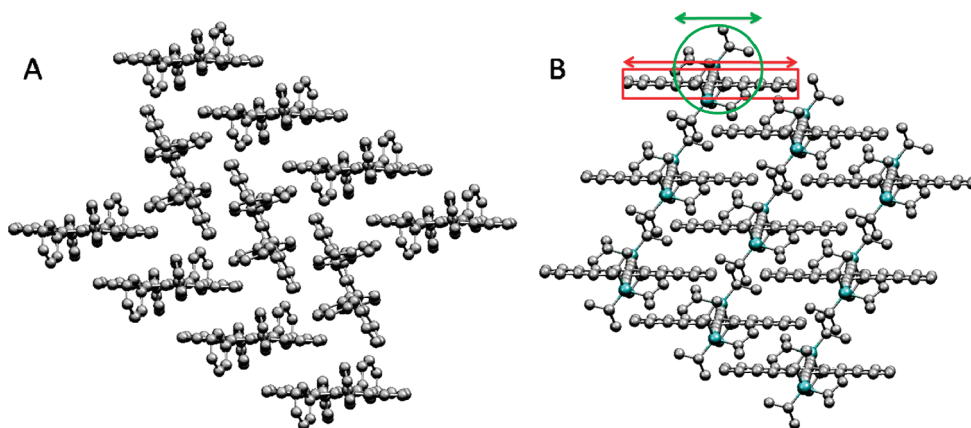


Figure 7. Utilizing substitution in the peri-positions of acenes in order to introduce π – π interactions. (A) Rubrene (RefCode QQQCIG11 from CSD); (B) TIPS-PEN (28d, Crystallographic data for 28d is provided as Supporting Information for ref 100).

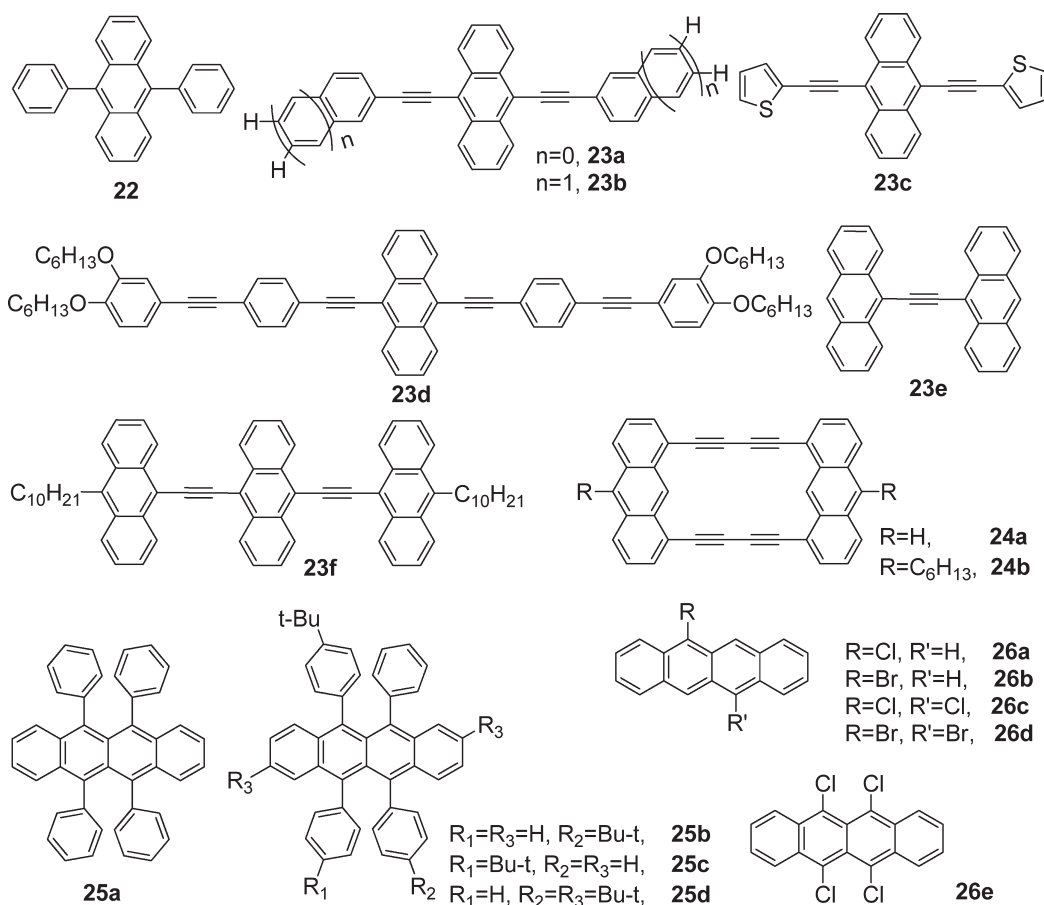
with substituents in the 1- and 8-positions. Single crystals of **24b** showed π – π intermolecular interactions. This suggests that these 1- and 8-substituents (also the peri-positions of anthracene) can lead to π -stacking similar to 9- and 10-substituents.

Just like their counterparts with substituents in the end-positions, tetracene derivatives with substituents in the peri-positions (**3a**) have not been studied extensively either. Rubrene (**25a**) is a representative compound and a benchmark for organic semiconductors.^{112,113} Although peri-position substituents result in poor planarity, they also, however, lead to strong π – π intermolecular interactions and a large π – π overlap (about one and a half benzene rings). This facilitates charge transport. Rogers et al.¹¹⁴ reported ground-breaking research of rubrene, wherein polydimethylsiloxane (PDMS), a very flexible elastomer, was used as the substrate. The low surface energy of PDMS favored intimate contact of the semiconductor/gate dielectric and the semiconductor/electrodes. Additionally, bottom contact configuration of the devices facilitated the examination of anisotropic charge transport of the rubrene crystals. It was found that the mobility of rubrene crystals was as high as $15.4 \text{ cm}^2/(\text{V}\cdot\text{s})$ along the *b* axis and $4.4 \text{ cm}^2/(\text{V}\cdot\text{s})$ along the *a* axis. Regardless of this high mobility of the rubrene single crystals, the thin films showed very low mobility (less than $10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$). This could be attributed to the poor planarity of the rubrene molecules which hinders the formation of crystalline films. High-quality rubrene thin films were successfully obtained when a pentacene buffer layer¹¹⁵ was introduced between the rubrene and the dielectric layers. Transistors of these films exhibited mobilities at $0.07 \text{ cm}^2/(\text{V}\cdot\text{s})$. Another method¹¹⁶ for obtaining rubrene films is to mix rubrene with an ultra high-molecular-weight (UHMW) polymer and a “glass-inducing” species in solution. The result is that the polymer provides good film-forming ability and excellent mechanical characteristics, and the vitrifying species acts as a diluent to hamper the crystallization of rubrene. Indeed, rubrene films generated using this method¹¹⁶ exhibited a mobility as high as $0.7 \text{ cm}^2/(\text{V}\cdot\text{s})$ with an on/off ratio at 10^6 . Recently, ambipolar field-effect transistors¹¹⁷ based on rubrene single crystals were also reported; they used Ag as source/drain electrodes. The hole and electron mobilities of rubrene were found to be 1.8 and $0.011 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively. Rubrene derivatives of 5,11-BTBR (**25b**)¹¹⁸ substituted by di-*t*-butyl groups were developed by Batlogg et al. There are two crystal phases for this compound. Transistors based on one phase exhibited no field-effect performance

due to the nonplanar structure of the tetracene core. The mobility of the other phase was similar to rubrene at about $12 \text{ cm}^2/(\text{V}\cdot\text{s})$. The tetra-*t*-butyl derivative (**25d**)¹¹⁹ of rubrene showed mobility at $10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$, much lower than **25c**. Recent research¹²⁰ suggests that halogen groups could introduce halogen–halogen intermolecular interactions, which in turn would promote molecular π -stacking in the crystals. A series of halogenated tetracene derivatives (**26a–d**)³⁶ were synthesized by Bao’s group. It was found that the number of substituents played an important role for molecular packing of the derivatives in the crystals. Monohalide derivatives (**26a,b**) showed a herringbone structure, while the dihalide (**26c,d**) displayed a slipped π stacking motif. Mobility of the compounds ranged from $1.4 \times 10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s})$ (**26b**) to $1.6 \text{ cm}^2/(\text{V}\cdot\text{s})$ (**26d**). The high performance of **26d** was probably due to its enhanced π -overlap a π -stacking arrangement. Crystals of tetrachlorotetracene (**26e**)¹²¹ had a large π – π overlap between its neighboring molecules, and its single crystal transistors exhibited a mobility as high as $1.7 \text{ cm}^2/(\text{V}\cdot\text{s})$.

Substituents of alkyl or aryl groups in the peri-position are expected to not only change the packing motifs (from herringbone to lamellar) but also improve the overall stability of the materials. Series of pentacene and tetracene derivatives with alkyl or aryl substituents (**27a,b**)^{122,123} were synthesized. When the pentacene substituents were changed from ethyl to propyl (at 1, 4, 6, 13 positions) the molecular packing motifs changed from herringbone to lamellar packing. For aryl substituted derivatives, the steric hindrance caused by the aryl groups was expected to block the herringbone packing so that π -stacking became available. This is similar to the effect of phenyl substitution in rubrene. The highest device performance was obtained from 6,13-di-(2'-thienyl)pentacene (**27b**) with a mobility at $0.1 \text{ cm}^2/(\text{V}\cdot\text{s})$. Anthony et al. hypothesized that the length ratio of the substituents and acene cores affected the packing of the materials.^{100,124,125} If the length of the substituents was approximately half the length of the acene core, the acene packing motif would change from herringbone to a lamellar structure (Figure 7B). Otherwise, a slipped π -stacking or herringbone packing structure could be adopted. For instance, the substituent lengths of **28b** ($\sim 5 \text{ \AA}$), **28c** (6.8 \AA), **28d** (TIPS-PEN, $\sim 7.5 \text{ \AA}$), and **28e** ($\sim 9 \text{ \AA}$) were close to half the length of pentacene ($\sim 7 \text{ \AA}$). The result is that they all adopted lamellar arrangements in single crystals. However, the shorter substituents ($\sim 4.3 \text{ \AA}$) of **28a** showed a slipped

Chart 5. Oligomers Based on Anthracene and Tetracene Substituted in the Peri-Positions



π -stacking.¹⁰⁰ These results are in good agreement with the hypothesis. Because of their 2-D *bricklayer* structure, **28d** vacuum-deposited films showed high OFET performance¹²⁵ with mobilities up to $0.4 \text{ cm}^2/(\text{V}\cdot\text{s})$. In fact, the mobility of its drop-casting films¹²⁶ could even reach $1.8 \text{ cm}^2/(\text{V}\cdot\text{s})$ with an on/off ratio over 10^7 , and self-assembled ribbons from solutions showed mobilities at $1.42 \text{ cm}^2/(\text{V}\cdot\text{s})$.¹²⁷ The tetramethyl substituted derivative (**28f**)¹²⁸ also showed a mobility as high as $2.5 \text{ cm}^2/(\text{V}\cdot\text{s})$ based on its solution-processed films. It is obvious that the stability and solubility of these derivatives are improved significantly because the alkyl substituents are introduced at the active center of the pentacene. Aromatic rings as substituents were also studied. It was found that the pentacene derivatives exhibited high solubility and stability. For example, Würthner et al. synthesized a series of acene derivatives with cores of anthracene (**29b**), tetracene, pentacene (**29a**), or anthradithiophene.¹²⁹ All compounds showed high solubility in common organic solvents. However, their spin-coated films showed very low mobility. The highest mobility of **29a** was obtained at around $10^{-5} \text{ cm}^2/(\text{V}\cdot\text{s})$. Although **29b** showed a lamellar structure in its crystals, vacuum deposited films showed mobility at $0.033 \text{ cm}^2/(\text{V}\cdot\text{s})$. Ong et al. developed a series of pentacenes derivatives (**29c**)¹³⁰ by altering the substituents at the benzene rings. The best performance of these compounds was obtained for the amyl derivatives. Its spin-coated films showed a mobility up to $0.08 \text{ cm}^2/(\text{V}\cdot\text{s})$, and drop-casted single crystalline micro/nanoribbons exhibited a mobility as high as $0.52 \text{ cm}^2/(\text{V}\cdot\text{s})$. Recently, in order to obtain 2D

isotropic charge transport,¹³¹ **30** was synthesized. Single crystals of **30** revealed that the two planes of the pentacene unit adopted a large twisting angle of about 78° . However, with a slipped $\pi-\pi$ stacking structure for both of them with those of the neighbor molecules, this suggests its potential for 2D isotropic charge transport. This cruciform pentacene derivative exhibited a mobility of $0.11 \text{ cm}^2/(\text{V}\cdot\text{s})$.

From a thorough analysis of the results, it is clear that substitution in the peri- or end-positions is one of the most important design strategies for the synthesis of acenes with high performance. This method is also very useful for heteroacenes (which will be discussed in section 3.1.2.1) and even for the design of oligomers. Substitution in the peri- (or side-) positions could tune the packing motifs from herringbone (edge-to-face) to $\pi-\pi$ stacking (face-to-face). As a result this would be expected to increase the transfer integrals and shorten the charge transport route, which in turn would facilitate charge transport. The different effects of the substituents in the peri- (or side-) positions and end-positions are summarized in Table 1.

Derivatives of acenes with substituents in the end- and peri-positions have been widely studied in OFETs. This research is stimulated by the expectation that substituents in the end-position can extend the π -system of acenes and substituents in the peri-position will improve their solubility. For instance, TIPSAntPV (**31c**) and TIPSAntHT (**31d**)¹⁵² both showed excellent solubilities with the result that the solution-processing can be used. In addition, their crystals displayed lamellar stacking

Chart 6. Oligomers Based on Pentacene Derivatives with Substituents in Peri-Positions

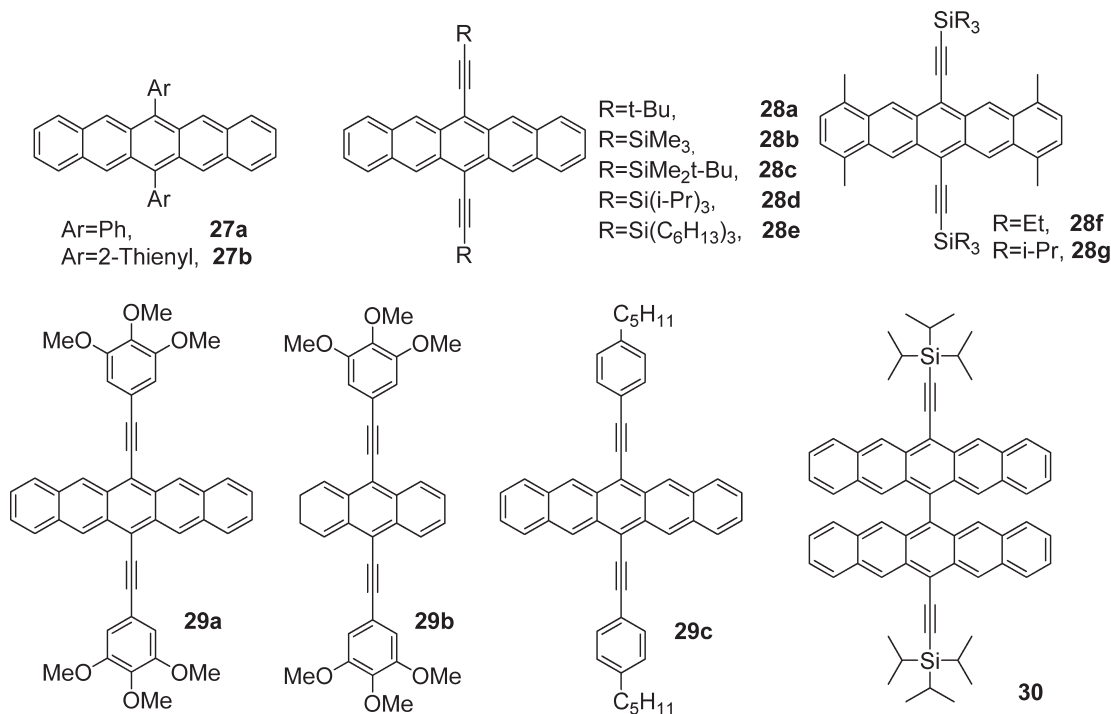


Table 1. Different Effects of the Substituents in Peri- (or Side-) Positions and End-Positions

position	aryl substituents					
	extending π -system	π - π stacking	planarity	crystallization	stability	alkyl substituents
peri-	favorable only when linked by carbon-carbon triple bonds	to prevent from C-H $\cdots\pi$ interactions, facilitate π - π stacking	favorable only when linked by carbon-carbon triple bonds	the nonplanar structure harms to crystalline films; strong π - π stacking facilitates crystals	to eliminate the active center	to improve the solubility and stability, increase π - π interactions
end-	favorable	unobvious effect	favorable	the planarity favors crystalline films	unobvious effect	to improve the solubility, unobvious effect on π stacking (51b)

with large π overlap. Similar results were obtained for OA-5b (**31a**)¹³³ and TIPSAntNa (**31b**).¹³⁴ Anthracene-based molecules with triple bond links in the 2, 6, 9 and 10-positions (**32a,b**)¹³⁵ were developed recently. Mobilities of 0.04 and 0.24 cm²/(V·s) were obtained for **32a** and **32b** based on their spin-coated films.

Although anthracene and its derivatives have been studied extensively in OFETs, phenanthrene (**2b**, the isomeric compound of anthracene) and its derivatives have been rarely examined. Recently, Geng's group synthesized a series of phenanthrene derivatives such as **33a,b**¹³⁶ and **33c**.¹³⁷ Field-effect transistors based on **33a** and **33c** showed mobility at 10⁻² cm²/(V·s). After optimization of the deposition conditions (to increase the substrate temperature up to 100 °C), transistors based on **33b** yielded a mobility as high as 0.12 cm²/(V·s) with an on/off ratio at 10⁵. Recently, a 9,10-dihydrophenanthrene derivative (**34**)¹³⁸ was synthesized by Bazan et al., which gave a mobility as high as 0.42 cm²/(V·s).

3.1.1.4. Other Aromatic Hydrocarbons. Similar to oligothiophene (which consists of a limited number of thiophene units in

contrast to polythiophene), oligophenyls were also studied as active layers for use in OFETs. Thin film transistors¹³⁹ based on thermally evaporated films of the oligophenyls (**35**), *p*-quaterphenyl (*p*-4P), *p*-quinquenphenyl (*p*-5P), and *p*-sexiphenyl (*p*-6P) were fabricated and showed mobilities in the range 10⁻²–10⁻¹ cm²/(V·s). These were equal to that found for oligothiophene (e.g., α -6T).¹⁴⁰ Gorjanc's group synthesized a double bond-linked oligophenyl derivative (**36c**)¹⁴¹ whose thin film transistors exhibited mobility at 0.094 cm²/(V·s) on SiO₂ substrates and 0.12 cm²/(V·s) on HMDS-modified substrates. Similarly, oligophenyl derivatives (**36a,b**)¹⁴² linked by vinylene groups were synthesized and examined in OFETs. Mobilities of 0.13 cm²/(V·s) for **36a** and 10⁻⁴ cm²/(V·s) for **36b**, respectively, were found. Recently, naphthalene end-capped divinylbenzene (**36d**)¹⁴³ was also synthesized and its thin film transistors exhibited mobility at 0.062 cm²/(V·s). Oligomers containing phenylene ethynylene units (**37**)¹⁴⁴ were also reported for use in OFETs. Transistors using **37a** as the organic active layer failed to show significant field-effect performance. However, with the incorporation of

Chart 7. Acene Derivatives with Substituents in Both Peri- and End-Positions

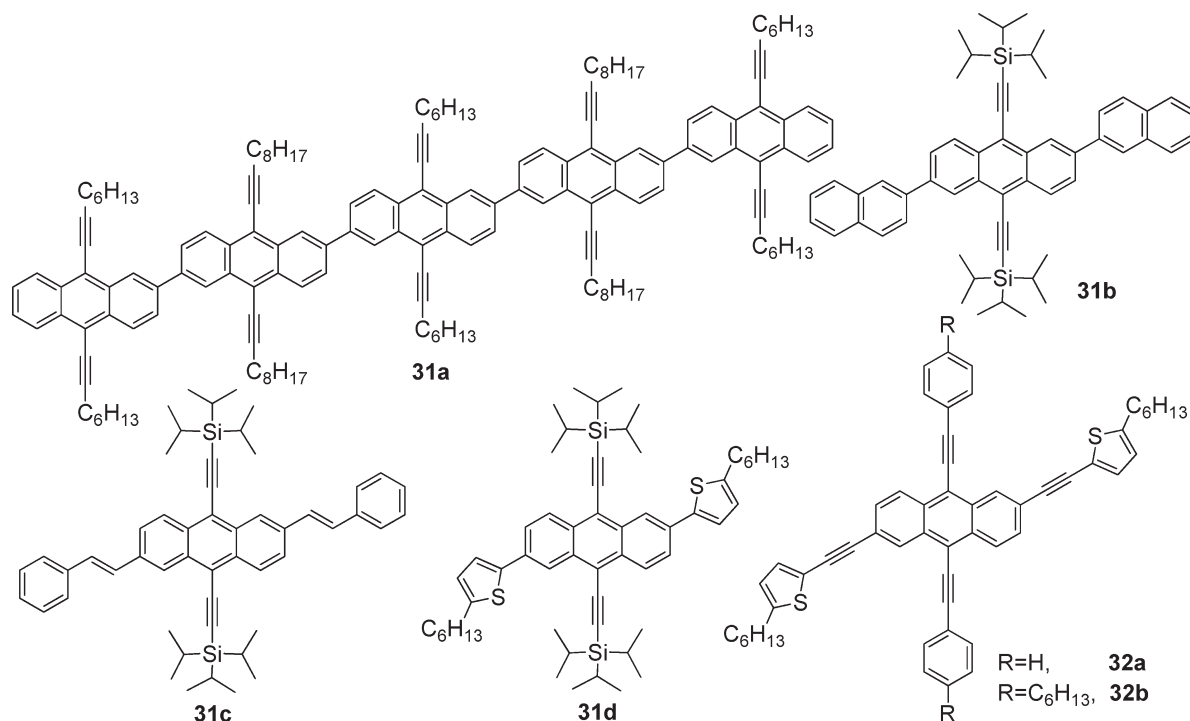
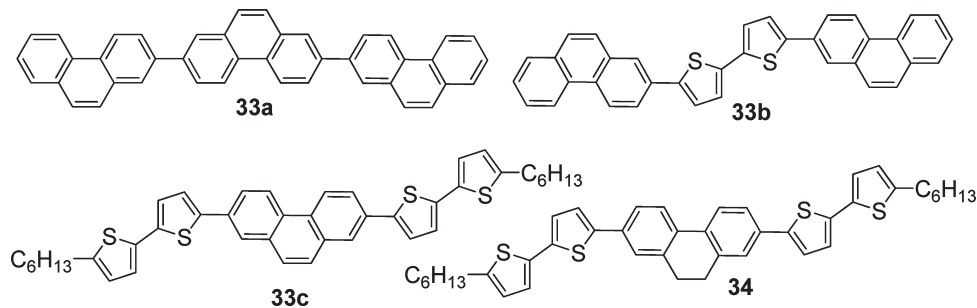


Chart 8. Oligomers Based on Phenanthrene



electron-donating groups, **37b** and **37c** exhibited mobilities at 0.3 and $3 \times 10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively. The performance of **37b** was much better than **37c**, which was attributed to **37b** having a less bulky trimethylsilyl group to be beneficial for ordered structures and charge transport.

Derivatives of fluorene are usually used as components of organic light-emitting diodes (OLED). Thin film transistors of oligofluorene derivatives^{145–150} combined with thiophene (**38a–g**) or thieno[3,2-*b*]thiophene(**38h**) exhibited mobilities over $10^{-2} \text{ cm}^2/(\text{V}\cdot\text{s})$. The highest mobility was observed in the OFETs of **38b** and **38d** at 0.17 and $0.12 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively. If the bithiophene unit was replaced by phenylene or biphenylene, another series of oligofluorene derivatives (**38i–k**)¹⁵¹ was obtained. The mobilities of **38i–k** were 0.06, 0.014, and $0.45 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively. Interestingly, these materials showed high stability, which is probably a result of their high ionization potential (low HOMO energy level about -5.6 to -5.7 eV). The **38k** devices did not exhibit significant degradation even after

being stored in air for 100 days. Oligofluorene derivatives (**38l–m**),^{152,153} substituted by alkyl groups in the fluorene 9-position, showed very low mobility (at 10^{-5} – $10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$). Asymmetric oligofluorene-thiophene molecules (**38n**)¹⁵⁴ showed mobility at $0.1 \text{ cm}^2/(\text{V}\cdot\text{s})$, which was better than **38l–m** but at the same level as those of the forementioned unsubstituted or dialkyl-substituted FTTF molecules. Thin films of the fused ring derivatives (**39a**)¹⁵⁵ displayed mobility at $0.012 \text{ cm}^2/(\text{V}\cdot\text{s})$, whereas the spin-coated films of more fused fluorene derivatives (**39b–d**)¹⁵⁶ showed a mobility of no more than $10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$.

3.1.2. Chalcogen-Containing Heterocyclic Semiconductors. The first material used in organic field-effect transistors was polythiophene which is based on a sulfur heterocyclic compound.¹² Since then, polymers, oligomers, and fused ring aromatic materials containing thiophene units have all been thoroughly examined. The rapid development of chalcogen-containing heterocyclic semiconductors can be explained by the following reasons. First, because of its similarity to the benzene ring, the

Chart 9. Oligophenyls

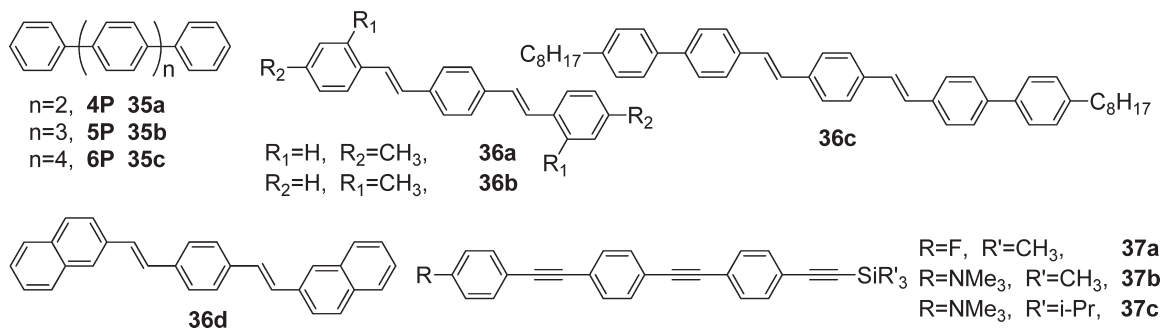
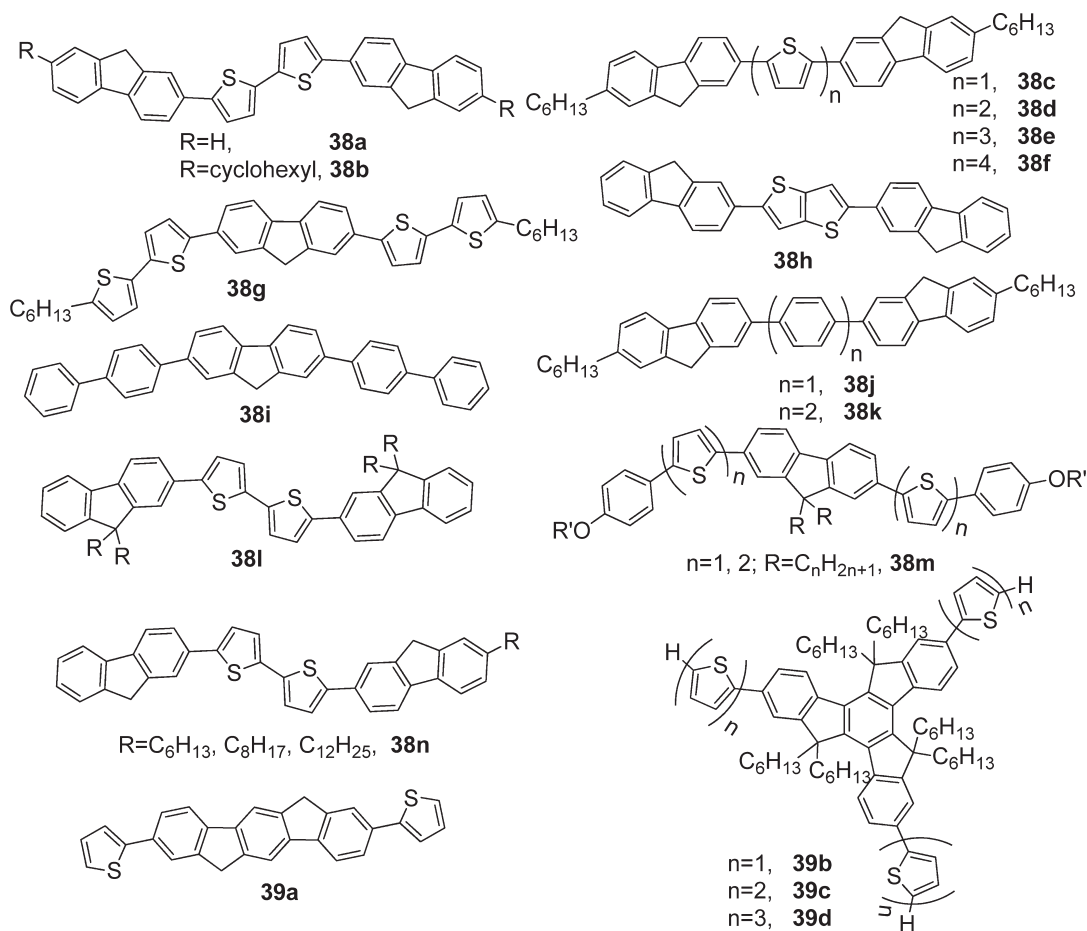


Chart 10. Derivatives Based on Fluorene



thiophene ring also has six π electrons ($4n+2$) and hence high aromaticity. Second, compared to the corresponding benzene-based materials, those containing thiophene units benefit from the fact that the molecules can pack in planar structures (e.g., polythiophenes or oligothiophenes).¹⁴⁰ Third, fused-thiophene-ring materials exhibit a much higher ability for antioxidation due to the absence of a Diels–Alder cyclization active center.¹⁵⁷ With the introduction of heteroatoms, even higher thienoacenes with six or seven fused aromatic rings exhibit excellent OFET performance and high stability. Finally, S atoms are able to introduce $S \cdots S$, $S \cdots H$, and $S \cdots \pi$ intermolecular interactions

(Figure 8) which enhance intermolecular interactions. This not only facilitates charge transport but also could change the packing motifs of the organic semiconductors, for example, from face-to-edge to face-to-face stacking. As a result, sulfur-containing materials have become one of the most important semiconductors for OFET applications. Oxygen-, selenium-, and tellurium-containing derivatives have all attracted a great deal of attention too.

3.1.2.1. Higher Thienoacenes. The application of pentathienoacene (PTA, **41**)¹⁵⁹ in OFETs was first reported by Liu's group. PTA is a pentacene analogue, which has a similar

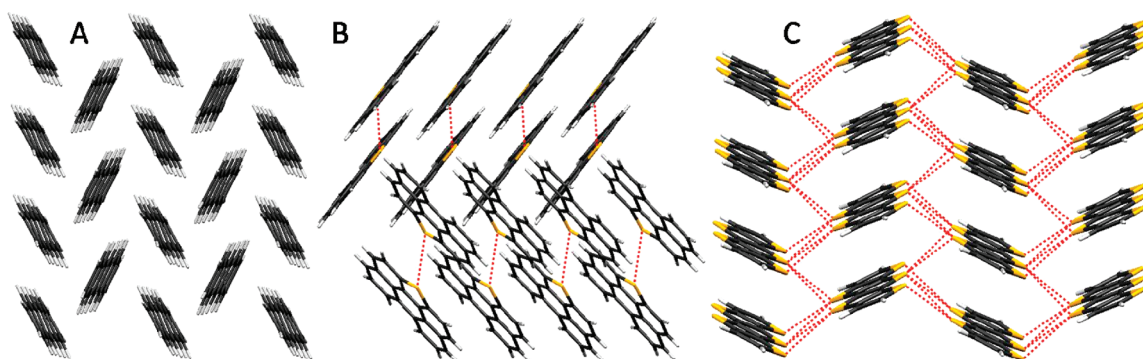


Figure 8. A possible route to increase π – π stacking: packing diagrams of (A) pentacene, herringbone packing driven by C–H $\cdots\pi$ interactions, (RefCode PENCEN from CSD); (B) PET (75a), slipped π – π stacking caused by chalcogen–chalcogen interactions (red dashed lines), (RefCode ROKQOX from CSD); and (C) PTA (41), slipped π – π stacking caused by high C/H ratios (diminished C–H $\cdots\pi$ interactions) and chalcogen–chalcogen interactions (red dashed lines), crystallographic data for 41 can be downloaded as Supporting Information for ref 158.

conjugation structure and π electrons to pentacene. However, the PTA HOMO energy level (–5.3 eV) was found to be lower than that of pentacene (–5.0 eV), and its energy gap (3.2 eV) was much larger than that of pentacene (1.8 eV). Because of these differences, PTA was more stable than pentacene in air. PTA crystals adopted a slipped π – π stacking arrangement which again was different from that of pentacene (Figure 8A,C). This can be attributed to the chalcogen–chalcogen interactions between the molecules and the high C/H ratios of PTA preventing C–H $\cdots\pi$ interactions and favoring π – π interactions. Recently, a series of thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene (40a) derivatives (40b–d)¹⁶⁰ with aromatic substituents showed mobilities larger than 0.1 cm²/(V·s) together with ideal solubility and environmental stability were reported. It was found that fused thiophenes with rings of even up to seven (42)¹⁵⁸ or eight units (43)¹⁶¹ still exhibited much better stability than the benzene-based analogues. Anthradithiophenes (ADT, 44a) are analogous to pentacene with thiophene instead of benzene as the end-capped rings. They showed greater antioxidation ability than pentacene. Moreover, although ADT was usually a mixture of syn- and anti- isomers, its vacuum evaporated films showed a mobility up to 0.09 cm²/(V·s). Alkylation of the reactants yielded several soluble anthradithiophene derivatives (44b–e).^{157,162} The vacuum evaporated films of 44b–e exhibited mobilities as high as 0.1 cm²/(V·s). In order to avoid a mixture of syn- and anti-isomers as in the case of 44, anthrathiophene (45a), and tetraceno[thiophene] (TCT, 46a)^{163,164} with only one thiophene ring as the end-capped groups were synthesized. The resulting compounds both showed lower HOMO energy levels and larger band gaps than those of pentacene. This indicates their higher stability than pentacene. Thin film OFETs of 45a and 46a showed mobilities of 0.15 and 0.47 cm²/(V·s), which were similar to pentacene under the same condition (0.5 cm²/(V·s)). For comparison, 46b with long alkyl side-chains and bromo (45c and 46d) and hexyl (45b and 46c) substituted derivatives¹⁶⁵ were also examined. Mobilities for these compounds were 45b at 0.12, 45c at 0.18, 46b at 0.064 cm²/(V·s), 46c at 0.23, and 46d at 0.79 cm²/(V·s), respectively. It is interesting to note that with the increase in conjugation length from 45 to 46, the average mobility increased from 0.12 to 0.23 cm²/(V·s) for the hexyl-substituted compounds (from 45b to 46c) and from 0.18 to 0.79 cm²/(V·s) for the brominated compounds (from 45c to 46d). OFETs of 2-fluorotetraceno[2,3-*b*]thiophene (46e)¹⁶⁶ showed an average

mobility of 0.3 cm²/(V·s). Recently, a hexacene analogue pentaceno[2,3-*b*]thiophene (47)¹⁶⁷ was synthesized by Bao's group. It showed much higher stability than hexacene, and its thin film OFETs exhibited a mobility as high as 0.574 cm²/(V·s). By replacing two or three benzene rings of pentacene with thiophene rings, compounds 48a–b¹⁶⁸ were synthesized by Neckers et al. They found that the benzene rings played an important role in the stability of such thienoacenes. Recently, heteroacenes with more fused thiophene rings¹⁶⁹ were synthesized by tailoring the alkyl substituents. It was found that dip-coated films of hexyl substituted derivative (49) gave a mobility as high as 1.7 cm²/(V·s) and an on/off ratio up to 10⁷.

Thienoacenes with benzene end-capped rings are also widely studied. For example, alkylated benzo[thieno[3,2-*b*]benzothiophene (BTBT) derivatives (50a)¹⁷⁰ were found to be highly soluble in common organic solvents, and their spin-coated films showed mobilities over 0.1 cm²/(V·s). The derivatives with C₁₃H₂₇ alkyl chains gave the highest device performance with mobilities as high as 2.75 cm²/(V·s) and on/off ratios of up to 10⁷. Vacuum evaporated films of the compounds showed even higher mobility than those of solution-processed ones;¹⁷¹ for example, a mobility of 3.9 cm²/(V·s) was observed for derivatives with C₁₂H₂₅ alkyl chains on ODTs-modified SiO₂/Si substrates. Changing the alkyl chains to phenyl groups showed that the compounds actually kept their high OFETs performance. For example, the benzo[thieno[3,2-*b*]benzothiophene derivative (50b)¹⁷² vacuum-evaporated films exhibited mobilities as high as 2.0 cm²/(V·s) and on/off ratios of up to 10⁷. Moreover, no obvious degradation was observed for 50b devices after 250 days. This indicates its extremely high stability for potential applications. Although derivatives of benzoselenopheno[3,2-*b*]benzoselenophene (BSBS) (50c) showed good field-effect performance, they were not as good as that of the diphenyl substituted derivatives (50d).^{172,173} 50d exhibited a mobility up to 0.31 cm²/(V·s), and after long-term continuous operation (3000 scans) and long-term storage (12 months) under ambient conditions, the devices showed no obvious degradation. BSBS derivatives¹⁷⁴ with alkyl chains (C_n-BSBS, 50e) showed mobilities of about 0.066–0.16 cm²/(V·s), respectively. Vinyl-BTBT derivatives (50f,g)¹⁷⁵ were also synthesized, and 50f showed a mobility at 0.024 cm²/(V·s), while the phenyl end-capped derivative (50g) exhibited mobility as high as 0.437 cm²/(V·s). Recently, two naphthodithiophene derivatives¹⁷⁶ (50h,i) were examined in OFETs and the mobility was 0.3 and 0.7 cm²/(V·s), respectively. Benzo[1,2-*b*:4,5-*b'*]bis[*b*]benzothiophene

Chart 11. Thienoacenes End-Capped by Thiophene Rings

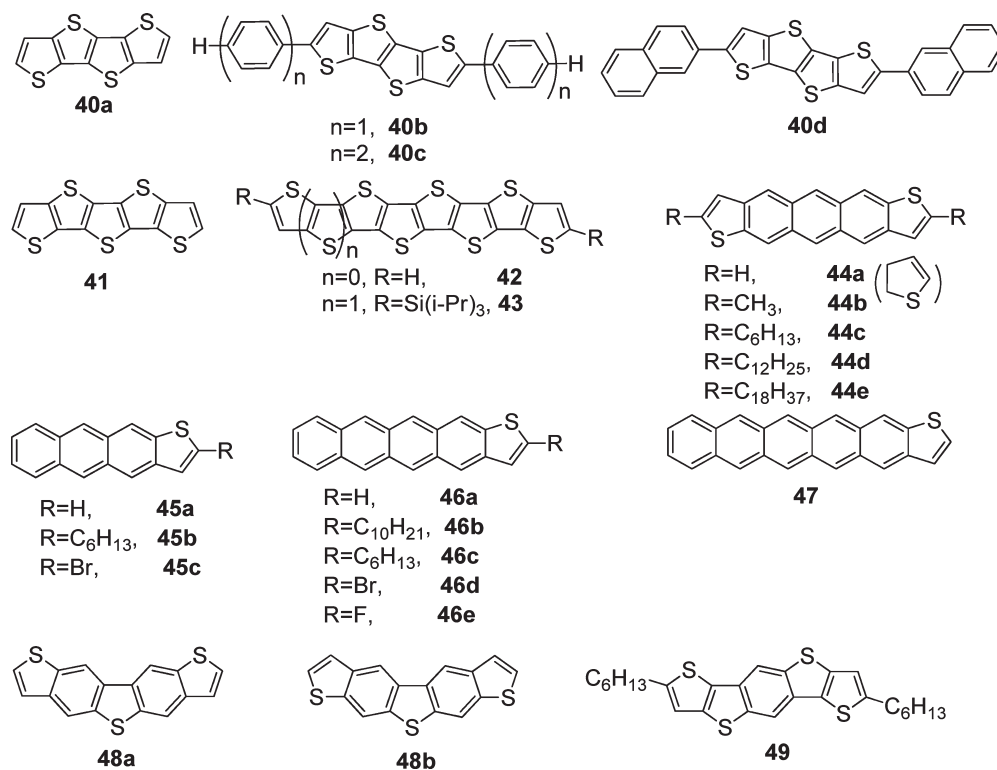
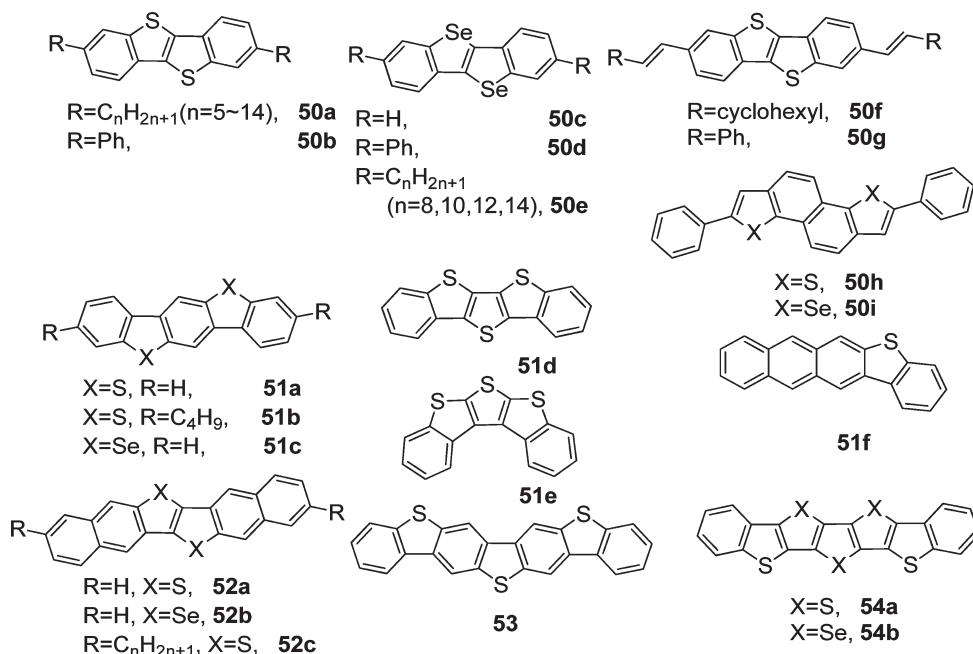


Chart 12. Thienoacenes End-Capped by Benzene Rings



(**51a**) and its butyl substituted derivative (**51b**)^{177,178} were synthesized efficiently. Interestingly, a lamellar structure was observed in crystals of **51b**, although the butyl groups were in the end-position instead of the peri- (or side-) position (Figure 9). It is believed that alkyl groups can change the packing

motif irrespective of their position; however, a lamellar structure is rarely observed in the crystals of acenes or heteroacenes with substituents in the end-positions. It is a pity that drop-casted films of **51b** exhibited lower mobility (10^{-3} cm²/(V·s)) than that of **51a** (10^{-2} cm²/(V·s)) for unknown reasons.

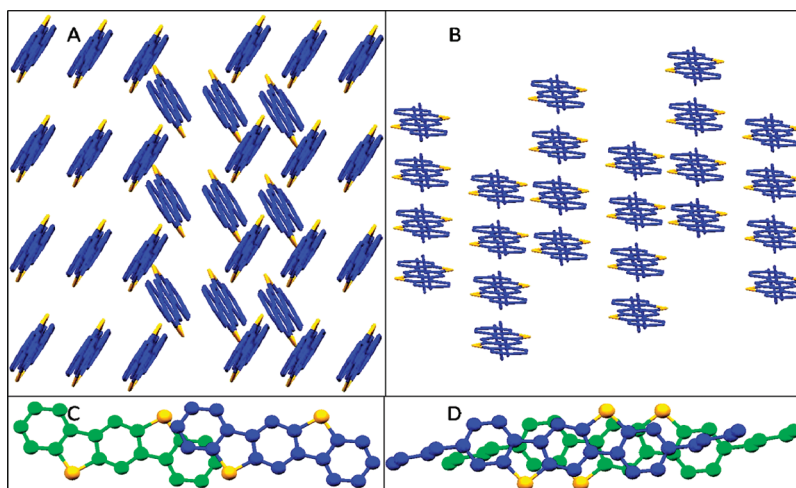


Figure 9. Top: crystal packing diagram of (A) **51a**, herringbone structure with weak π - π stacking and (B) **51b**, lamellar structure, 1D π -stacking. Bottom: π -overlap between neighboring molecules of (C) **51a** and (D) **51b**, viewed perpendicularly to the plane of the core. Protons are omitted for clarity. Crystallographic data for these compounds can be downloaded as Supporting Information for ref 178.

Selenium-containing pentacene analogues (**51c**) also showed low mobility ($3 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$) irrespective of whether they were on OTS or HMDS-modified SiO_2/Si substrates. Dibenzo[*d,d'*]-thieno[3,2-*b*;4,5-*b'*]dithiophene (DBTDT, **51d**)¹⁷⁹ was synthesized by Hu's group using a facile synthesis route. The HOMO energy level of DBTDT was about -5.6 eV (much lower than pentacene) and its energy gap was at about 3.46 eV (almost twice that of pentacene). This suggests DBTDT possesses good stability. The DBTDT thin films showed mobilities as high as $0.5 \text{ cm}^2/(\text{V}\cdot\text{s})$ with an on/off ratio of up to 10^6 . On the other hand, DBTDT single crystals demonstrated mobility as high as $1.8 \text{ cm}^2/(\text{V}\cdot\text{s})$ ¹⁸⁰ as a result of the molecules adopting a typical herringbone packing. However, BBTT (**51e**),¹⁸¹ which is an isomer of DBTDT, adopted a slipped π -stacking instead of the herringbone packing in its single crystals. This is probably due to the sickle-like shape of the BBTT molecules which prevented $\text{C}-\text{H}\cdots\pi$ interactions between neighboring molecules in the side-positions. OFETs of BBTT single crystals exhibited a mobility at $0.6 \text{ cm}^2/(\text{V}\cdot\text{s})$. One noteworthy result is the fact that another asymmetric molecule, anthra[2,3-*b*]benzo[*d*]thiophene (ABT, **51f**),¹⁸² showed a similar high performance to BBTT with its thin film mobility at $0.41 \text{ cm}^2/(\text{V}\cdot\text{s})$. This supports the prospect of using asymmetrical thienoacenes in OFETs. Moreover, both BBTT and ABT exhibited high stability, without obvious degradation even after 3 months of storage in air.

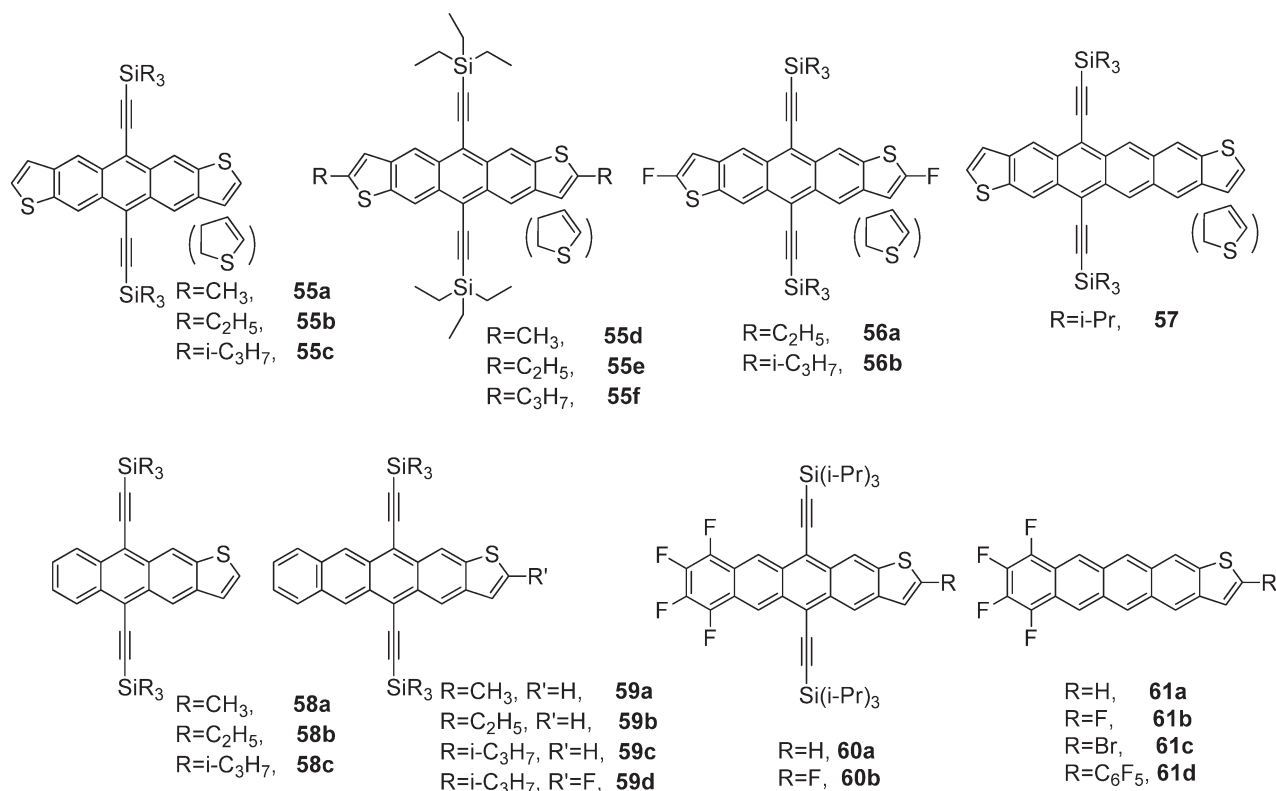
With the introduction of heteroatoms, the higher thienoacenes with six or seven fused aromatic rings were synthesized and examined in OFETs. High device performance was demonstrated based on studies using these compounds. For example, DNNT (**52a**),¹⁸³ which has six fused aromatic rings, exhibited mobility up to $2.9 \text{ cm}^2/(\text{V}\cdot\text{s})$ and an on/off ratio of 10^7 based on vacuum-sublimated films on OTS-treated SiO_2/Si substrates. Again, single crystals¹⁸⁴ showed mobility as high as $8.3 \text{ cm}^2/(\text{V}\cdot\text{s})$ with an on/off ratio of up to 10^9 . Its subthreshold slopes using Cytop-treated SiO_2 as dielectrics and gold/TTF-TCNQ as top-contacted electrodes were found to be 0.4 V/decade . Similarly, the selenium-containing hexacene analogue (**52b**) showed a mobility as high as $1.9 \text{ cm}^2/(\text{V}\cdot\text{s})$, and **52c** (C_{10} -DNNT)¹⁸⁵ films gave mobilities as high as $8.0 \text{ cm}^2/(\text{V}\cdot\text{s})$. These results indicate that the strategy of introducing

heteroatoms for the synthesis of organic semiconductors with high mobility is highly effective.

Sirringhaus et al. reported a heptacene analogue (**53**)¹⁸⁶ which has three kinds of isomers that were hard to separate from each other. By properly controlling the deposition conditions, most of the sublimated material obtained was identified as **53**, and transistors based on its films showed mobility as high as $0.15 \text{ cm}^2/(\text{V}\cdot\text{s})$, while films with mixed isomers exhibited a mobility of only about $0.03 \text{ cm}^2/(\text{V}\cdot\text{s})$. Another heteroacene with seven fused aromatic rings (**54a**)¹⁸⁷ was obtained by Yamaguchi et al. OFETs of its single crystals¹⁸⁸ exhibited a mobility of $0.5 \text{ cm}^2/(\text{V}\cdot\text{s})$ together with excellent device stability. The selenium-containing derivative (**54b**) exhibited a mobility of $1.1 \text{ cm}^2/(\text{V}\cdot\text{s})$, which was about twice as high as that of the corresponding sulfur-containing derivatives (**54a**).

Similar to acene derivatives, the thienoacene derivatives substituted by trialkylsilylacetylene groups in the peri-position have also been widely studied. On the one hand, these substitutions can improve the stability and increase the solubility of the materials, whereas on the other hand, the peri-position could hamper the formation of $\text{C}-\text{H}\cdots\pi$ intermolecular interactions and facilitate π - π interactions. Anthony et al. synthesized a series of trialkylsilylacetylene functionalized anthradithiophene derivatives (**55**)¹⁸⁹ from their anthradithiophenequinone precursors. They obtained a mixture of syn- and trans- compounds, of which the trimethylsilyl derivative **55a** showed a typical herringbone arrangement. The triethylsilyl derivative **55b** adopted a 2D π -stacking, and the triisopropylsilyl derivative **55c** displayed a 1D slipped packing motif. Solution-processed films⁶ of **55a** and **55c** showed poor FET performance, and the mobility of **55c** was found to be only $0.05 \text{ cm}^2/(\text{V}\cdot\text{s})$. However, the **55b** devices showed mobilities as high as $1.0 \text{ cm}^2/(\text{V}\cdot\text{s})$ based on drop-casted films. Derivatives of thienoacenes with substituents on the thiophene rings (**55d-f**)¹⁹⁰ were also developed. Interestingly, **55d** adopted 1D stacking in crystals and exhibited a mobility at $0.1-0.4 \text{ cm}^2/(\text{V}\cdot\text{s})$ from its solution-cast films. Although 1D and 2D π -stacking were observed for **55e** and **55f**, based on their solution deposited films very low mobilities were obtained. This is probably due to their poor morphology and weak intermolecular interactions (π - π distance as large as

Chart 13. Trialkylsilylacetylene Substituted Derivatives of Thienoacenes



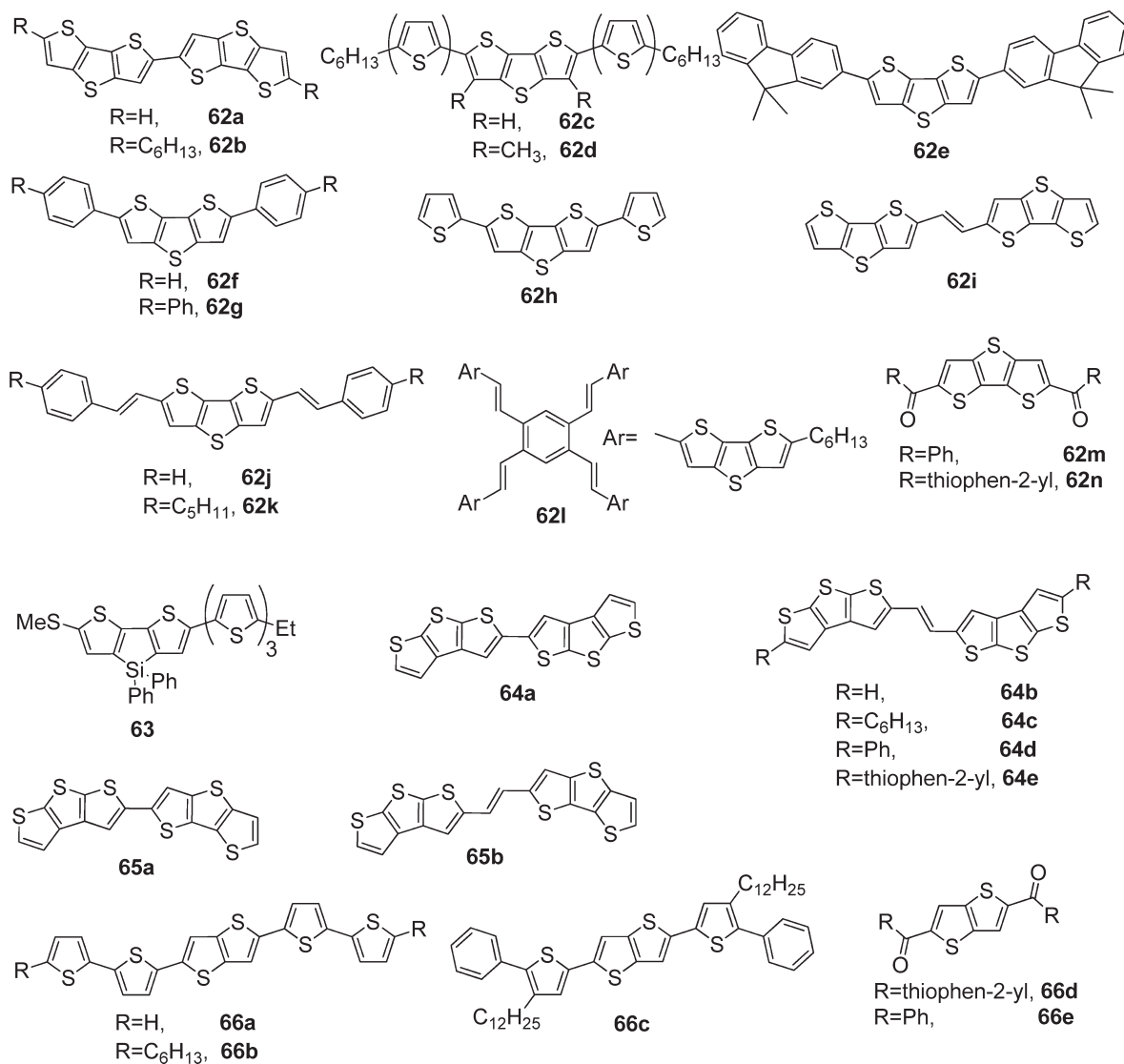
3.8 Å). Fluorinated anthradithiophene derivatives (**56a,b**)¹⁹¹ were also obtained in the form of an inseparable mixture of syn- and anti-isomers. F···F and F···S noncovalent interactions were observed in these crystals, and the resulting enhanced intermolecular interactions indeed improved the FET performance. Spin-coated films of **56a** showed maximum mobility of 1.5 cm²/(V·s) and an average mobility of 0.7 ± 0.15 cm²/(V·s). These were significantly larger than the corresponding values for the nonfluorinated derivatives (**55b**). Single crystal OFETs¹⁹² of **56a** were also fabricated and showed mobilities as high as 6 cm²/(V·s) with on/off ratios of 10⁸. Acenedithiophenes with up to six fused rings substituted by trialkylsilylacetylene groups (**57**) have also been reported. Although this derivative exhibited good solubility and strong π - π interactions in its crystals, its solution-processed films exhibited poor FET behaviors (10⁻⁵ cm²/(V·s))⁶. A class of trialkylsilylethynyl substituted anthra[2,3-*b*]thiophene (**58**) and tetraceno[2,3-*b*]thiophene (**59**) derivatives¹⁹³ were developed by Bao et al. The substitutions in the peri-position also induced π -stacking in the crystals. Vacuum deposited films of **59c** showed a mobility as high as 1.25 cm²/(V·s). This was attributed to its 2D π -stacking molecular arrangement. Interestingly, ambipolar behaviors were found in the fluorinated tetraceno[2,3-*b*]thiophene derivatives (**59d**, **60**–**61**).^{166,194} Evaporated films of **60a** under nitrogen in a glovebox showed electron and hole mobilities at 0.37 cm²/(V·s) and 0.065 cm²/(V·s), respectively. When tested under an ambient atmosphere, the hole mobility increased to 0.12 cm²/(V·s) and the on/off ratio increased by 2 orders of magnitude. Vacuum deposited films of **59d** and **60b** also showed a hole mobility at 0.3 cm²/(V·s) with lower electron mobilities of 0.04 and 0.1 cm²/(V·s), respectively. OFETs of **61a,b,d** did not

demonstrate high mobility, although ambipolar FET performance was observed (**61c** showed no FET behavior).

It is obvious that the introduction of chalcogen atoms increases the stabilities of the higher thienoacenes; for example, analogues of hexacene and heptacene that contain six or seven fused rings exhibit super device performance. Moreover, chalcogen–chalcogen intermolecular interactions could further enhance π - π interactions for molecular stacking (e.g., from pentacene to pentathienoacene as shown in Figure 8), and the strategy of introducing substitution in the side-positions of acenes also proved useful for tuning the molecular arrangement of the thienoacenes.

3.1.2.2. Oligomers of Thienoacenes. As mentioned in the previous section, oligomers of the smaller thienoacenes (containing a core with two or three fused rings, such as naphthothiophene, dithienothiophene, benzodithiophene, dibenzothiophene, thienothiophene, or benzothiophene) are expected to possess high solubility and stability. Although α,α' -bis(dithieno[3,2-*b*:2',3'-*d'*]thiophene (BDT, **62a**)^{195,196} and its dihexyl substituted BDT derivative (DH-BDT, **62b**),¹⁹⁷ dithienothiophene with bithiophenes (**62c**)^{150,198} and the dimethyl substituted derivative (**62d**)¹⁹⁹ all exhibited mobilities of only 10⁻² cm²/(V·s), the derivatives that combined dithienothiophene with fluorene (**62e**) showed even low mobility. However, oligomers of **62f**–**h**²⁰⁰ demonstrated mobilities as high as 0.42, 0.12, and 0.14 cm²/(V·s), respectively. It was found that derivatives end-capped with phenyl and biphenyl groups showed high stability under ambient conditions. For instance, the device developed using **62g** maintained mobility at about 0.1 cm²/(V·s) even after 9 weeks. Recently, styryl end-capped derivatives²⁰¹ were also synthesized. The oligomers based on trithiophene **62j** showed a

Chart 14. Oligomers with Smaller Thienoacenes (Dithienothiophenes and Thienothiophenes)



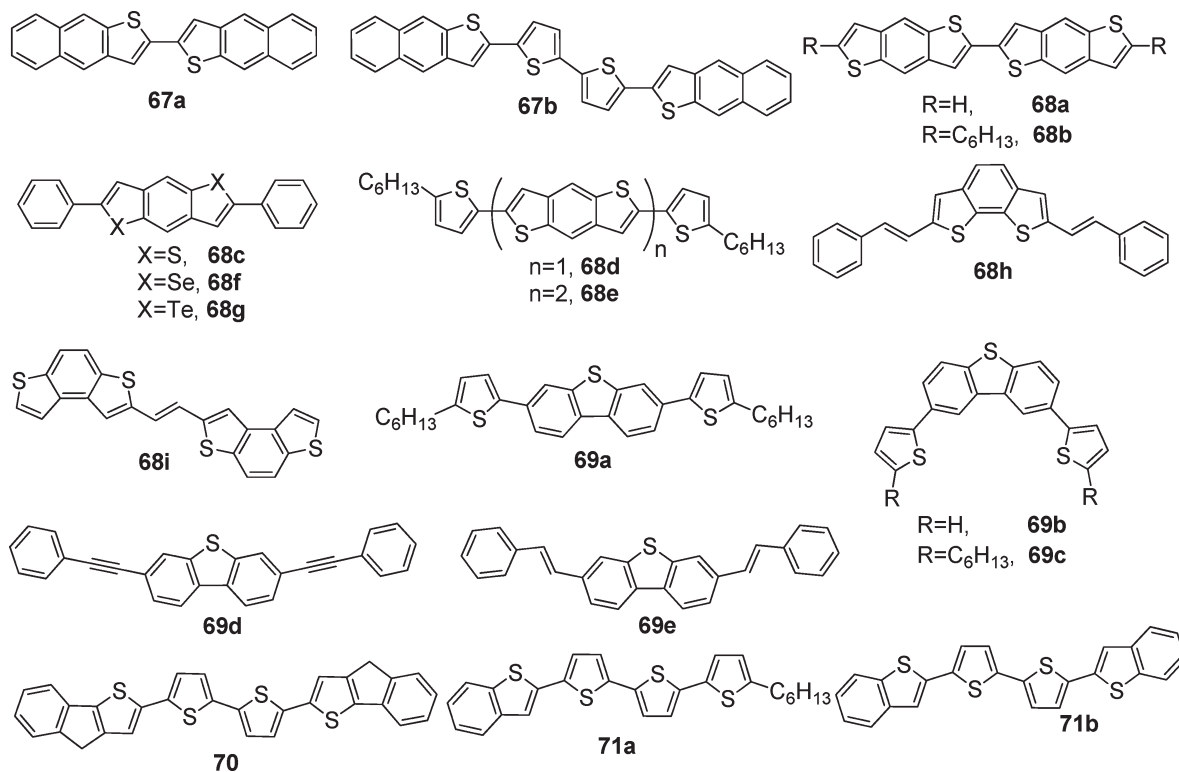
mobility of $0.17 \text{ cm}^2/(\text{V}\cdot\text{s})$, which was about one order higher than that of the alkylated derivative **62k** and those of thienothiophene or the **40a**-based counterparts. Choi's group²⁰² synthesized a series of soluble star-shaped molecules based on thiophene derivatives using Horner–Emmons reactions (e.g., **62l**). However, the compounds exhibited low mobilities. Dithienosilole units were developed to enhance molecular conjugation. Unfortunately, the oligomers²⁰³ containing the dithienosilole units were not as active as expected and **63** showed only a very low mobility. A class of derivatives²⁰⁴ based on dithienothiophene (**62m,n**) and thienothiophene (**66d,e**) linked by carbonyl groups was also developed. Compounds showed p-channel performance but the highest mobility was only $0.01 \text{ cm}^2/(\text{V}\cdot\text{s})$ (**62m**).

Derivatives^{205,206} containing β -trithiophenes are very interesting. The single bond-linked derivatives (**64a**) showed a mobility of $5 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$. This was one order lower than that of the α -trithiophenes-based derivatives (**62a**). However, the double bond-linked derivatives (**64b**) exhibited mobilities as high as $0.89 \text{ cm}^2/(\text{V}\cdot\text{s})$ with on/off ratios of up to 10^7 , and these are

10 times those of the vinylene-bridged α -trithiophenes dimer (**62i**) ($0.08 \text{ cm}^2/(\text{V}\cdot\text{s})$) and oligomer (**65**).²⁰⁷ Oligomers end-capped with phenyl groups (**64d**) showed mobilities even as large as $2.0 \text{ cm}^2/(\text{V}\cdot\text{s})$ and on/off ratios of up to 10^8 . In addition, devices based on these compounds showed high environmental stability. No obvious degradation was observed after storing in air for seven months. Some other oligomers, such as **66a–e**, based on thienothiophene were also investigated. Thin films of **66a,b**²⁰⁸ exhibited p-type behaviors with mobility of $0.12 \text{ cm}^2/(\text{V}\cdot\text{s})$ and the spin-coated films of **66c**²⁰⁹ showed mobility at $0.03 \text{ cm}^2/(\text{V}\cdot\text{s})$.

OFETs with [2,2']bi[naphtho[2,3-*b*]thiophenyl] (BNT, **67a**)⁴⁴ as the active layer showed a mobility of $0.67 \text{ cm}^2/(\text{V}\cdot\text{s})$ in air. The HOMO energy level of BNT was found to be about -5.73 eV . In principal, BNT should match with a Au (-5.1 eV) electrode better than with the TTF-TCNQ complex (-4.64 to -4.78 eV). However, transistors using TTF-TCNQ as the source and drain electrodes exhibited much higher mobility than those devices using Au as the electrodes. This is probably due to the better contact between the organic semiconductor and the organic electrode. The oligomer combining the

Chart 15. Oligomers with Other Smaller Thienoacenes



naphtho[2,3-*b*]thiophenyl unit and the bithiophene unit (**67b**), in which the two terminal thiophene rings of the quaterthiophene (**4T**) are replaced by two naphtho[2,3-*b*]thiophenyl groups,²¹⁰ showed a mobility of 0.01 cm²/(V·s) on PMMA-treated Ta₂O₅ substrates. This was higher than that for **4T** under the same conditions (2×10^{-3} cm²/(V·s)).

The benzodithiophene unit as a building block was also examined in organic semiconductors. The benzodithiophene building block derivatives (**68a**),²¹¹ its dihexyl substituted oligomer (**68b**), and the diphenyl substituted derivative (**68c**)²¹² all exhibited mobilities about 10⁻² cm²/(V·s). In addition, the casting films of **68d** and the vacuum deposited films of **68e** displayed mobilities at about 10⁻³ cm²/(V·s).²¹³ Interestingly, 2,6-diphenylbenzodiselenophene (**68f**) exhibited a higher mobility (up to 0.17 cm²/(V·s)) than its sulfur-containing counterpart **68c** (up to 0.081 cm²/(V·s)). The on/off ratio was found to have increased by 2 orders of magnitude. However, the 2,6-diphenylbenzoditellurophene (**68g**)²¹² exhibited lower mobility at 7.3×10^{-3} cm²/(V·s). The syn-isomer (**68h**)²¹⁴ which is approximated by a "kite" shape showed a mobility up to 0.1 cm²/(V·s) on HMDS-modified SiO₂/Si substrates. Another series of benzodithiophene-based derivatives²¹⁵ was also synthesized. The highest performance was obtained from **68i** with a mobility of 0.02 cm²/(V·s).

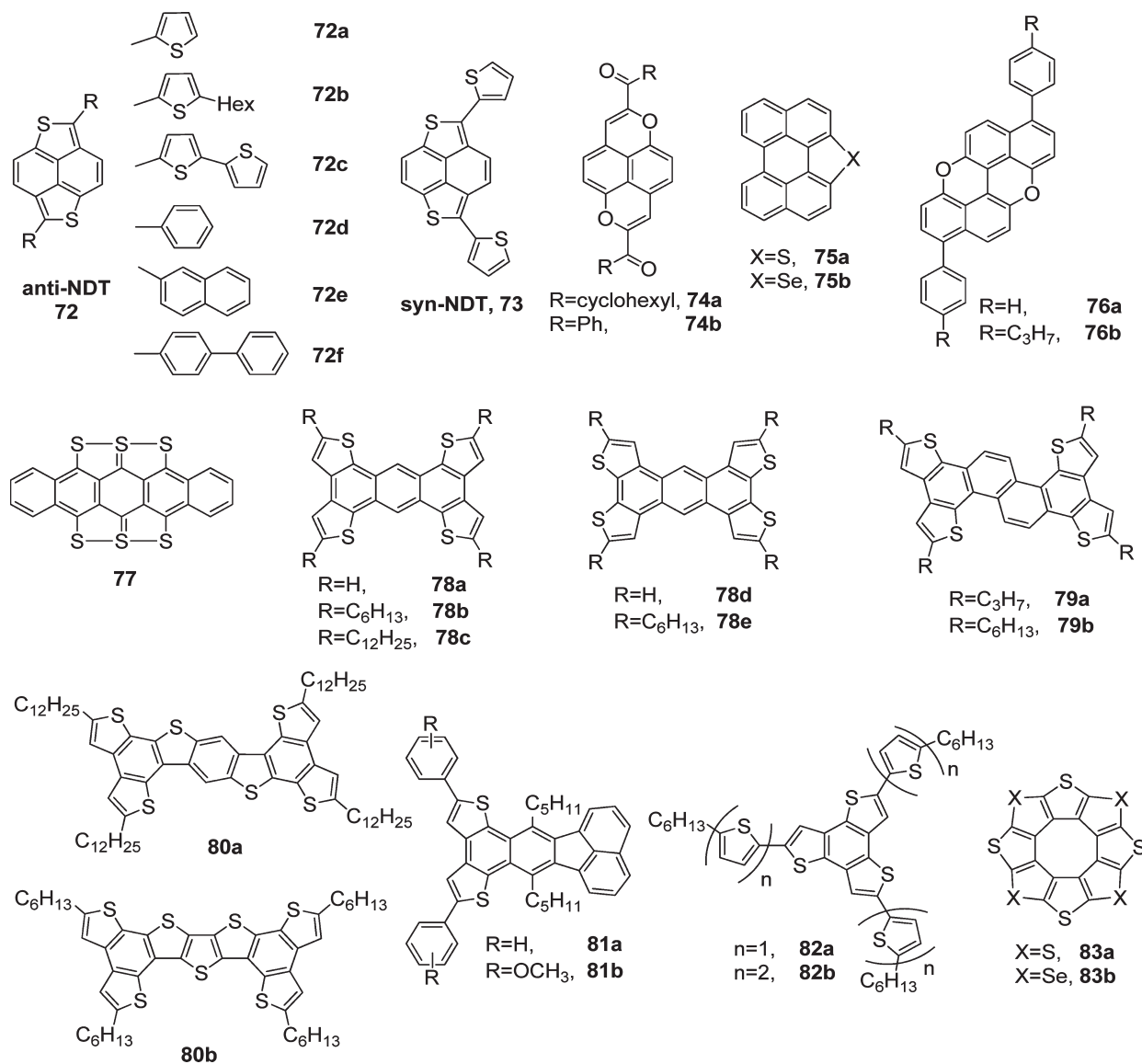
Dibenzothiophene (DBT) is another small unit containing three rings which also has high ionization potential. Its derivatives are expected to give high stability. Hu's group found that the 3,7-substituted oligomers (**69a**) showed more extended π -systems than the 2,8-substituted (**69b,c**) DBT derivatives.²¹⁶ Mobility for **69a** was at 0.077 cm²/(V·s), which was much higher than found for **69b,c**. Further studies²¹⁷ of dibenzothiophene derivatives with carbon-carbon unsaturated bonds (**69d,e**) substituted in the 3- and 7-positions are also reported. The

vacuum deposited films of **69e** showed a mobility of 0.15 cm²/(V·s), which was almost 3 orders of magnitude higher than that of **69d**. Quaterthiophenes (**70**)²¹⁸ based on a central bithiophene core and α,ω -terminated with indeno[1,2-*b*]thiophene were synthesized using either Stille or Miyaura-Suzuki coupling reactions and its transistors gave a mobility of 2.2×10^{-2} cm²/(V·s). This was comparable to the similar fluorene-based oligomer (**38a**) and naphtho[2,3-*b*]thiophenyl-based oligomer (**67b**). Compounds of **71a** and **71b**²¹⁹ end-capped benzothiophene units showed mobility at about 0.011 cm²/(V·s) on PMMA-treated Ta₂O₅ substrates.

3.1.2.3. Fused Aromatic Chalcogen-Containing Compounds. Two isomeric fused heteroarenes (the NDT derivatives, **72** and **73**)^{220,221} which are isoelectronic with pyrene were developed by Takimiya et al. Compared to pyrene, the HOMO energy levels of NDT were greatly increased, whereas the LUMO energy levels were lowered due to the aromatic character being reduced by the loss of the Kekulé benzene rings in the skeleton. The thienyl substituted anti-NDTs (**72a,b**) showed rather low mobilities (at 10⁻⁴ cm²/(V·s)), and no field-effect performance was observed for the syn-NDT derivative (**73**). However, other derivatives (**72c-f**) substituted in the 2,6-positions displayed mobilities over 10⁻² cm²/(V·s). The highest performance was obtained for **72e** with the mobility as high as 0.11 cm²/(V·s). Two peri-condensed heteropyrenes (**74**)²²² containing oxygen atoms were examined by Shukla et al. These 1,6-dioxapyrene derivatives were very stable and formed well-ordered polycrystalline films with ease. Results revealed a hole mobility as high as 0.25 cm²/(V·s) for **74a** and 0.1 cm²/(V·s) for **74b**, respectively.

Two chalcogen-heterocyclic perylene derivatives (**75**) were synthesized by Wang's group. Strong chalcogen-chalcogen and π - π intermolecular interactions (as shown in Figure 8B for **75a**)

Chart 16. Fused Aromatic Chalcogen-Containing Compounds



were observed in the single crystals of perylo[1,12-*b,c,d*]thiophene (PET, **75a**)²²³ and perylo[1,12-*b,c,d*]selenophene (**75b**).²²⁴ Single crystal transistors based on an individual assembled micro-wire of **75a** showed a mobility up to 0.8 cm²/(V·s). It is worth noting that individual microribbon of selenium-containing derivative **75b** exhibited a mobility as high as 2.66 cm²/(V·s). Kobayashi et al. synthesized both 3,9-diphenyl-*peri*-xanthoxanthene (**76a**, Ph-PXX) and 3,9-bis(*p*-propylphenyl)-*peri*-xanthoxanthene (**76b**, PrPh-PXX).²²⁵ OFETs based on vacuum deposited Ph-PXX films showed mobilities over 0.4 cm²/(V·s), and no significant degradation was observed after 5 months of storage in ambient conditions. PrPh-PXX exhibited a mobility as high as 0.81 cm²/(V·s) for its vacuum deposited films and 0.43 cm²/(V·s) for solution-processed films. Single crystals of hexathiapentacene (HTP, **77**)²²⁶ showed strong S···S intermolecular interactions (3.37–3.41 Å). However, the mobility of HTP was only at 0.005–0.04 cm²/(V·s).

A series of tetrathienoacenes was synthesized by Pei et al. Here the acene cores were anthracene (**2a**), chrysene (**3b**) and

benzo[1,2-*b:4,5-b'*]bis[*b*]benzothiophene (**51a**), which provided the compounds **78a–e**,^{227,228} **79**,²²⁹ and **80**,²³⁰ respectively. The vacuum evaporated films of **78b** showed a very low mobility of 10^{−4} cm²/(V·s). However, the mobility increased to 0.012 cm²/(V·s) after thermal annealing at 230 °C for 20 min. Peregichka's group showed that the isomeric hexylated compounds **78e** exhibited higher mobility (0.074 cm²/(V·s)) than **78b**. Interestingly, alkyl functionalized chrysene derivatives (**79a**, **b**) exhibited a mobility as high as 0.4 cm²/(V·s) based on their vacuum deposited films. In addition, the benzo[1,2-*b:4,5-b'*]bis[*b*]benzothiophene derivative (**80a**) showed good self-assembly characteristics. Transistors based on individual microwires via slow crystallization²³¹ showed typical p-channel behavior with a mobility of 2.1 cm²/(V·s). Crystalline nanoribbons of **80b**²³² formed through solution self-assembly also exhibited excellent performance with a mobility of 0.42 cm²/(V·s). A series of similar sulfur-heterocyclic benzo[*k*]fluoranthene derivatives (**81**)²³³ were also synthesized. The methoxyl substituted derivatives (in the *o*-, *m*-, *p*-positions) (**81b**) all showed mobilities

around $10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$, even after annealing. However, the mobility of the annealed films of **81a** reached $0.083 \text{ cm}^2/(\text{V}\cdot\text{s})$ with an on/off ratio of 10^6 . Planar star-shaped oligothiophenes (**82**)²³⁴ with benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophene as the core were synthesized by Blanchard et al. OFETs²³⁵ based on thermal evaporated films of **82b** showed mobility of $10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$. Sunflower (**83**)^{236,237} shaped thienoacene derivatives were also prepared. OFETs using **83a** as semiconducting layers exhibited mobilities of about $9 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$. On the other hand, the tetrathiotetraseleno[8]circulene (**83b**)²³⁷ provided a maximum mobility of $1 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$, about 10-fold lower than that of **83a**.

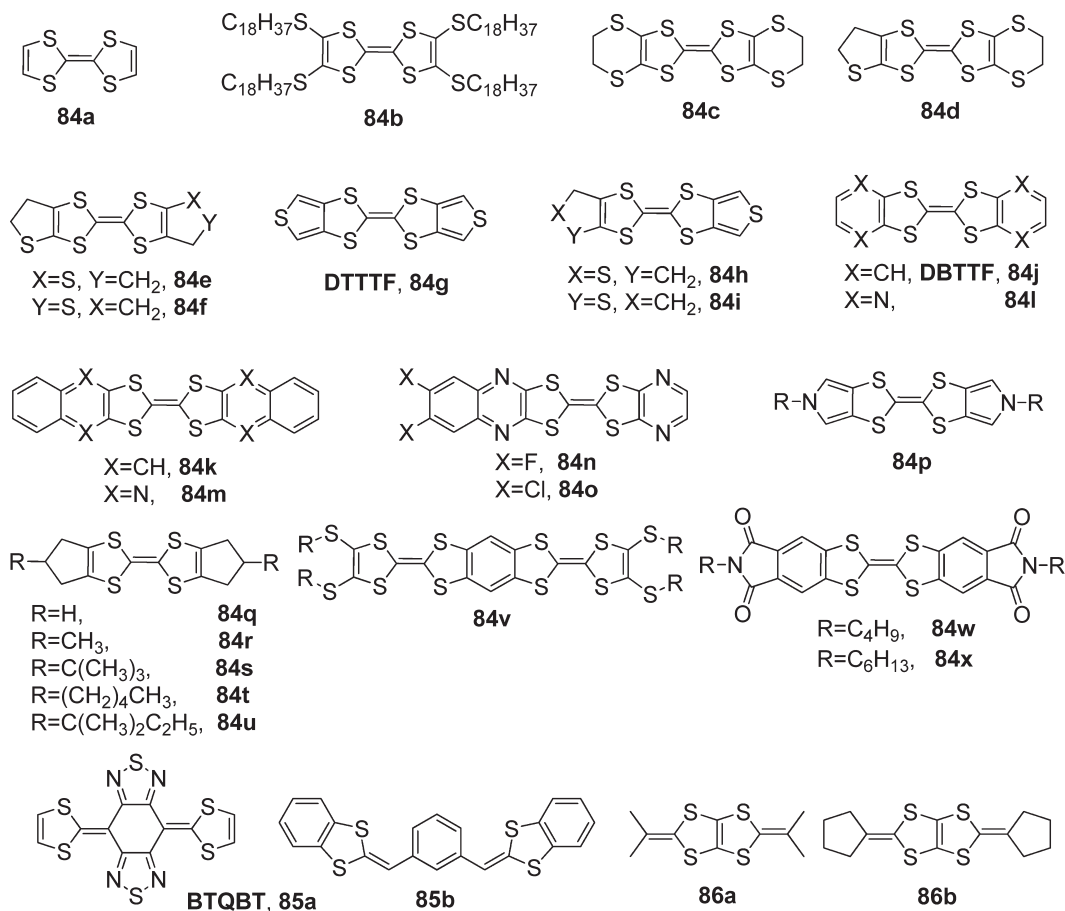
3.1.2.4. TTF and Its Derivatives. Tetrathiafulvalene (TTF, **84a**) and its derivatives have been widely studied as organic conductors and superconductors (see special reviews^{9,238}). In 1993, TTF derivatives²³⁹ were first used as semiconducting layers for field-effect transistors. Crystals of TTF have two phases. It was found that the crystals which belonged to monoclinic α -TTF ($1.2 \text{ cm}^2/(\text{V}\cdot\text{s})$)²⁴⁰ exhibited higher mobility than those belonging to triclinic β -TTF ($0.23 \text{ cm}^2/(\text{V}\cdot\text{s})$). This was attributed to the strong π -stacking along the *b* axis in the α phase. Through a solution-processed technique known as zone-casting, OFETs based on aligned films of TTF-4SC18 (**84b**)²⁴¹ were fabricated and showed mobility up to $0.08 \text{ cm}^2/(\text{V}\cdot\text{s})$ with on/off ratios of about 10^4 . Mas-Torrent et al. examined a series of TTF derivatives (**84c–j**).^{242,243} Single crystals of **84g** (DT-TTF)²⁴⁴ exhibited mobilities up to $1.4 \text{ cm}^2/(\text{V}\cdot\text{s})$ (recently a mobility as high as $3.6 \text{ cm}^2/(\text{V}\cdot\text{s})$ was also reported²⁴⁵). Single crystals of **84j** (DB-TTF)²⁴⁶ displayed mobility in the range of $0.1–1 \text{ cm}^2/(\text{V}\cdot\text{s})$. A series of π -extended TTF derivatives (**84k–o**)²⁴⁷ were synthesized by Yamashita et al. Thin films of **84k** on ODTS-treated SiO_2 substrates showed a hole mobility of $0.42 \text{ cm}^2/(\text{V}\cdot\text{s})$, and **84m** exhibited mobility of $0.2 \text{ cm}^2/(\text{V}\cdot\text{s})$ on Al_2O_3 substrates. The dihalogen derivatives (**84n–o**)²⁴⁸ showed mobilities of $0.2 \text{ cm}^2/(\text{V}\cdot\text{s})$ for **84n** and $0.64 \text{ cm}^2/(\text{V}\cdot\text{s})$ for **84o**, respectively. Mobilities of these compounds were higher than the corresponding unsubstituted derivatives which might be attributed to the stronger intermolecular interactions promoted by the dihalogen groups. Takimiya et al. synthesized a class of N-alkyl-substituted bis(pyrolo[3,4-*d*])tetrathiafulvalenes (PyTTF, **84p**)²⁴⁹ and the device performance of the compounds proved less than ideal. The highest performance was obtained from the spin-coated films of cetyl and icosyl substituted derivatives with mobility of $0.013 \text{ cm}^2/(\text{V}\cdot\text{s})$ and an on/off current ratio about 10^4 . Fortunately, Takahashi and co-workers²⁵⁰ recently reported another TTF derivative (HMTTF, **84q**) with extremely high mobility. Transistors using its single crystals employing thermally evaporated TTF-TCNQ films as the source/drain electrodes exhibited mobilities over $10 \text{ cm}^2/(\text{V}\cdot\text{s})$. The high performance was attributed to the close side-by-side and brickwork packing (2D lamellar arrangement) and the ideal contact between HMTTF and the TTF-TCNQ electrode. Inspired by such pioneer work, a class of HMTTF derivatives (**84r–u**)²⁵¹ were synthesized by Mori et al. Thin film transistors of HMTTF exhibited mobility up to $3.6 \text{ cm}^2/(\text{V}\cdot\text{s})$. Transistors based on **84s–u** also showed high mobilities at 0.98, 0.19, 0.60 $\text{cm}^2/(\text{V}\cdot\text{s})$, respectively. Liu's group reported a series of thioalkyl group substituted dimeric TTFs (**84v**).^{252,253} Their spin-coated films showed a mobility of $0.02 \text{ cm}^2/(\text{V}\cdot\text{s})$. In fact, perylene diimides and naphthalene diimides are typical n-type semiconducting materials. However, the dibenzotetrathiafulvalene (DBTTF) bisimides (**84w–x**)²⁵⁴ showed good p-type characteristics because of the electron-rich properties of the TTF core. The butyl (**84w**) and hexyl (**84x**) group substituted derivatives showed a hole

mobility of $0.094 \text{ cm}^2/(\text{V}\cdot\text{s})$ and $0.4 \text{ cm}^2/(\text{V}\cdot\text{s})$ with an on/off ratio of up to $10^6–10^8$.

The sulfur containing bis(1,2,5-thiadiazolo)-*p*-quinobis(1,3-dithiole) (BTQBT, **85a**)^{255,256} has the TTF units separated by a cyclohexane unit. By optimizing the growth conditions, BTQBT films showed a hole mobility as high as $0.2 \text{ cm}^2/(\text{V}\cdot\text{s})$ with an on/off ratio of up to 10^8 . The Hall mobility²⁵⁷ of BTQBT single crystals was determined to be $4 \text{ cm}^2/(\text{V}\cdot\text{s})$. By inserting conjugated spacers such as N-methylpyrrole, furan, thiophene, and benzene with *meta* (**85b**) or *para* linkages, between two dithiafulvalenyl moieties, Frère's group developed a series of TTF derivatives.²⁵⁸ The highest OFET performance was obtained from **85b** with a mobility of $0.081 \text{ cm}^2/(\text{V}\cdot\text{s})$. Bando et al. obtained a tetrathiapentalene (TTP) derivative (**86**)²⁵⁹ occasionally. Transistors based on its vacuum deposited films on HMDS-modified SiO_2/Si substrates showed a mobility at $0.27 \text{ cm}^2/(\text{V}\cdot\text{s})$. This was very close to the results obtained using TTF-TCNQ as the source and drain electrodes in bottom-contact configurations ($0.17 \text{ cm}^2/(\text{V}\cdot\text{s})$).

3.1.2.5. Oligothiophenes. Both the first OFET and the first printed transistor utilized polythiophenes as their semiconducting layers.^{18,260,261} Oligothiophenes in particular have attracted attention since the discovery of OFETs because (i) oligothiophenes facilitate planar structures rather than nonplanar structures as occurs in oligophenyls (planar structures are possible under particular conditions), (ii) it is much easier to modify thiophene than benzene rings. Taking the molecule α -6T²⁶² as an example, its mobility is improved from $10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s})$ to $0.1 \text{ cm}^2/(\text{V}\cdot\text{s})$ within the past few decades, and that of octithiophene (α -8T, **87d**)^{263,264} reaches up to $0.28 \text{ cm}^2/(\text{V}\cdot\text{s})$. The quaterseleophene (**87e**, 4S)²⁶⁵ was synthesized by a Stille coupling reaction and showed a mobility of $3.6 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$, equal to quaterthiophene (**87a**, 4T). Usually, with the expansion of the conjugated system, the solubility of the oligomers would be expected to decrease. This is a disadvantage where the synthesis and purification of materials is concerned. In addition, their application in solution-processed techniques (drop-casting, dip-coating, spin-coating, inkjet printing, etc.) required for the fabrication of their devices and circuits is compromised. Therefore, the introduction of alkyl chains is essential for the design of organic semiconductors with high solubility. It is facile to modify thiophenes at the 2,5-positions; moreover, substitution here will improve the stability of the resulting oligomers. Hence, the alkylated oligomers (**88a–n**)²⁶⁴ have been widely studied. Moreover, many studies²¹⁹ showed that judicious substitution of alkyl groups improves the field-effect performance of organic compounds. For example, quaterthiophene and sexithiophene derivatives²⁶⁶ end-capped with alkyl groups exhibited higher transistor performance than their unsubstituted counterparts; for example, mobility increased from 2.5×10^{-3} to $0.03 \text{ cm}^2/(\text{V}\cdot\text{s})$ for quaterthiophene (from **87a** to **88b**) and from 0.02 to $0.08 \text{ cm}^2/(\text{V}\cdot\text{s})$ for sexithiophene (from **87c** to **88j**), respectively. Additionally, structure–property relationship studies suggest that the molecules probably adopt arrangements with their long axis perpendicular to the substrates for the alkylated oligothiophenes. This highly ordered molecular arrangement was found to result in higher OFETs performance, and the mobilities increased more than 10-fold. Although the unsubstituted oligothiophenes^{267–269} usually showed a mobility lower than $0.1 \text{ cm}^2/(\text{V}\cdot\text{s})$, most of the derivatives end-capped with alkyl groups²⁷⁰ exhibited mobilities larger than $0.1 \text{ cm}^2/(\text{V}\cdot\text{s})$. The diethyl (**88i**) and dihexyl (**88j**) substituted sexithiophene

Chart 17. TTF and Its Derivatives

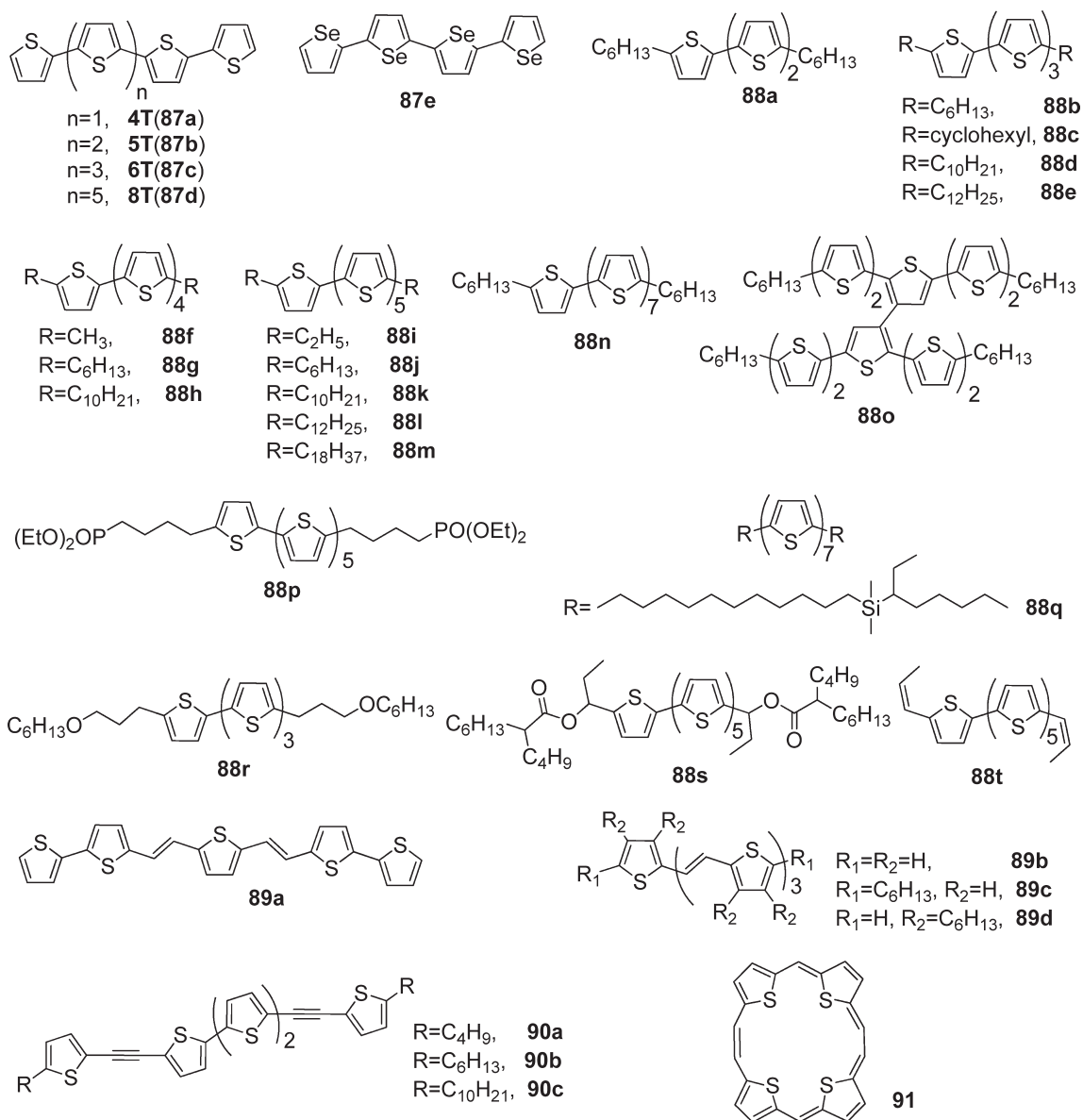


derivatives²⁶⁴ gave mobilities as high as 1.0 and 1.1 $cm^2/(V \cdot s)$. Besides the linear alkyl groups, cycloalkyl groups have also been introduced into the molecular structures. It was found that the quaterthiophene with cyclohexyl end-capping groups (**88c**, 0.038 $cm^2/(V \cdot s)$)¹⁴⁷ showed a little higher mobility than that with hexyl groups (**88b**, 0.02 $cm^2/(V \cdot s)$).²⁷¹ This is coincident with the results for the fluorene derivatives of **38b** and **38d**, and the drop-casting films of **88c** which exhibited an even higher mobility of 0.06 $cm^2/(V \cdot s)$. A lot of swivel cruciforms^{272–274} were also synthesized, but only very low OFET performance was observed because of the swiveling structures. The highest performance was shown by α, α' -dihexylpentathiophene (**88o**) with a mobility up to 0.012 $cm^2/(V \cdot s)$. Oligothiophenes with alkylphosphate (**88p**),²⁷⁵ alkylsilyl (**88q**),²⁷⁶ and alkoxy (**88r**)^{277,278} etc. as end-capping groups were also synthesized and the highest performance was obtained from **88q**²⁷⁶ with its mobility as high as 0.18 $cm^2/(V \cdot s)$. The spin-coated films²⁷⁹ of the diester-functionalized sexithiophene derivative **88s** showed only low mobility (10^{-5} $cm^2/(V \cdot s)$). After annealing at 200 °C for 20 min the mobility was improved up to 0.05 $cm^2/(V \cdot s)$. This was apparently caused by thermolysis to form compound **88t**. Oligothiophenes linked by carbon–carbon double bonds (**89a–d**)^{280,281} and **91**²⁸² and triple bonds (**90a–c**)^{283,284} were also examined recently. The derivatives **89a**²⁸⁰ showed mobility at 0.01 $cm^2/(V \cdot s)$ for molecular beam deposition (MBD) films and 0.001 $cm^2/(V \cdot s)$ for spin-coated films. The vacuum sublimated films²⁸¹ of **89b, c** showed mobility up to 0.0014 and 0.055 $cm^2/(V \cdot s)$, which was

much higher than those of the derivatives (**89d**) substituted in the peri-positions (3,4-positions of thiophenes). Tetrathia-[22]annulene[2,1,2,1] (**91**)²⁸² was synthesized by Zhu's group. It adopted a nearly planar structure and its evaporated films showed a mobility of 0.05 $cm^2/(V \cdot s)$. The self-organizing liquid-crystalline monodomain films^{283,284} of triple bond-linked molecules **90a–c** showed bipolar performance with a hole mobility of about 0.02 $cm^2/(V \cdot s)$ and an electron mobility of about 2×10^{-3} $cm^2/(V \cdot s)$.

Oligomers combined with thiophene and benzene rings have also been widely studied. The phenyl-capped quaterthiophene (**92a**)²⁸⁵ and quinquethiophene (**92b**)²⁸⁶ derivatives showed mobilities at 0.09 $cm^2/(V \cdot s)$ and 0.13 $cm^2/(V \cdot s)$ (single crystal devices). The biphenyl-capped trithiophene (**92d**) and quaterthiophene (**92e**) derivatives^{287–289} exhibited a mobility as high as 0.17 $cm^2/(V \cdot s)$. Moreover, ambipolar behaviors²⁹⁰ were observed for single crystals of **92d** with hole and electron mobilities as high as 1.64 and 0.17 $cm^2/(V \cdot s)$. **92c**²⁹¹ showed a mobility at 0.66 $cm^2/(V \cdot s)$ for polycrystalline films on KCl substrates, and naphthalene-end-capped quaterthiophene (**92f**)²⁹² demonstrated a mobility of 0.4 $cm^2/(V \cdot s)$. As for the 4-hexylphenyl end-capped oligothiophenes,²⁸⁸ the best performance was obtained for bithiophene (**92h**) and quaterthiophene (**92j**) derivatives with mobilities up to 0.09 $cm^2/(V \cdot s)$. Trithiophenederivatives (**92i**) displayed mobilities about 0.054 $cm^2/(V \cdot s)$. The similarly 4-methylphenyl substituted oligothiophenes (**92k–m**)²⁹³ provided a comparable performance with a mobility of about

Chart 18. Oligothiophenes



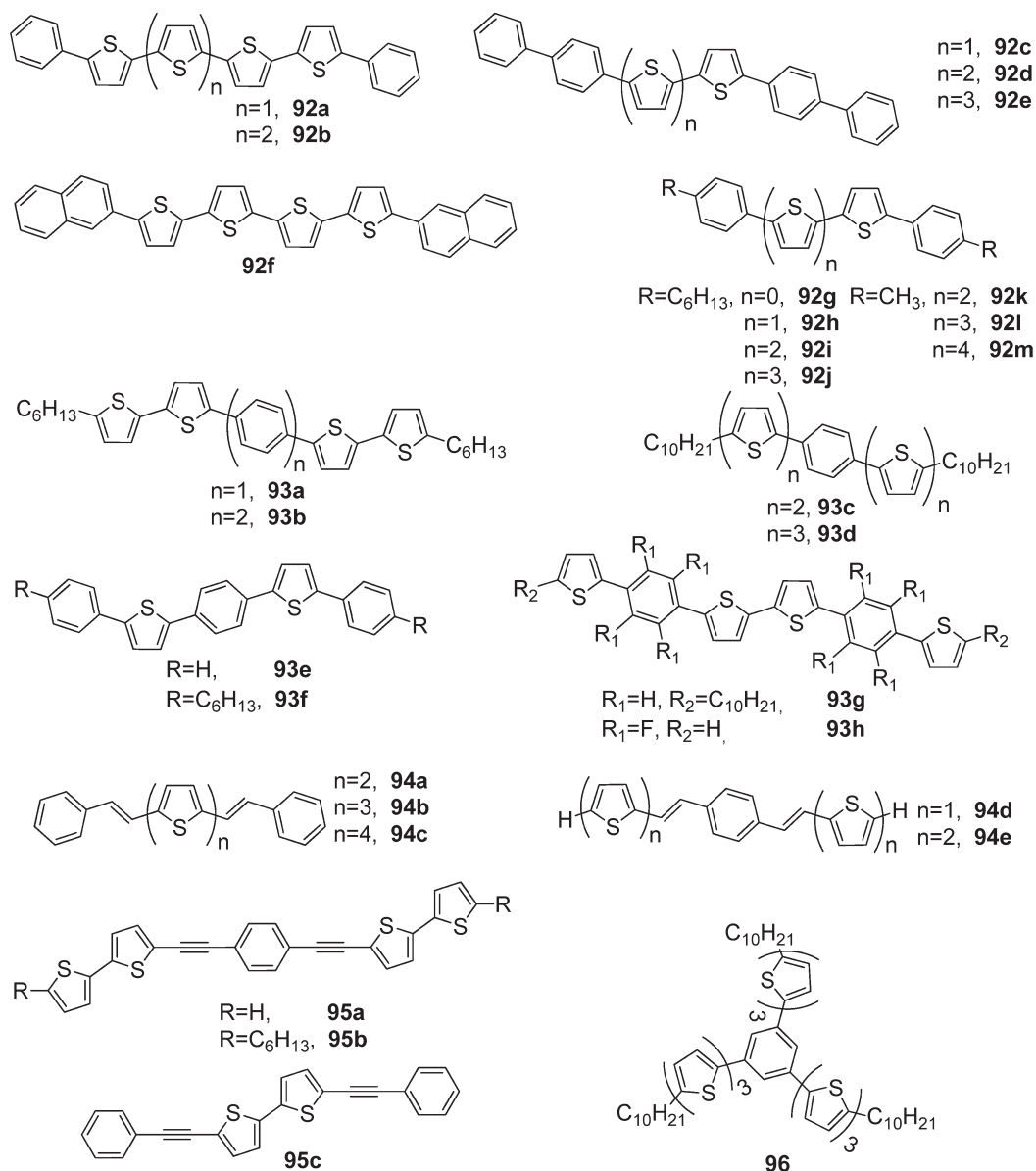
0.02–0.03 cm²/(V·s). The thiophene end-capped oligophenyls (**93c**)^{294,295} had values as high as 0.3 cm²/(V·s), while **93a,b**¹³⁷ and **93d** were lower at 10⁻² cm²/(V·s). Thiophene-phenylene co-oligomers **93e**,²⁹⁶ **93f**,²⁸⁸ and **93g**²⁹⁵ showed mobilities at about 0.02, 0.054, and 0.4 cm²/(V·s), respectively. The octafluorinated derivatives (**93h**)²⁸⁵ showed a hole mobility of 0.01 cm²/(V·s). The carbon–carbon double bond-linked oligomers also consisted of two kinds of structures with phenyl-capped (**94a–c**)²⁹⁷ and thiophene-capped (**94d–e**)²⁹⁸ counterparts. The oligomers end-capped with benzene rings showed a mobility of 0.02–0.1 cm²/(V·s), which were much better than the corresponding thiophene end-capped oligomers, for example, 10⁻⁷ cm²/(V·s) for **94d** and 6–7 × 10⁻³ cm²/(V·s) for **94e**. Devices based on triple bond-linked oligothiophenes (**95a–c**) were developed by Hu's group,²⁹⁹ and values of up to 0.056, 0.084, and 0.028 cm²/(V·s) were obtained. Although star-shaped molecules based on thiophene and benzene rings²³⁵ have also been widely studied, the mobilities obtained are not

always satisfying. For instance, transistors³⁰⁰ based on **96** showed a hole mobility of only 2 × 10⁻⁴ cm²/(V·s).

A perusal of the literature confirms that sulfur-containing semiconductors are widely used in OFETs. The introduction of sulfur or other chalcogen atoms into the relevant molecules will increase the stability of these compounds. In fact, some compounds are found with not only high air stability but also high mobility. Moreover, the introduction of chalcogen atoms always leads to chalcogen–chalcogen intermolecular interactions, which along with π – π interactions in crystals leads to overall enhanced intermolecular interactions which are beneficial for obtaining high device performance.

3.1.3. Nitrogen-Containing Heterocyclic Semiconductors. **3.1.3.1. Phthalocyanines and Porphyrins.** One type of nitrogen-containing heterocyclic semiconductor, the phthalocyanines are widely studied for applications in OFETs.^{301,302} Copper phthalocyanine (CuPc, **97b**), titanyl-phthalocyanine (TiOPc, **97k**), and vanadyl-phthalocyanine (VOPc, **97l**) are representative

Chart 19. Oligomers Based on Thiophene with Benzene

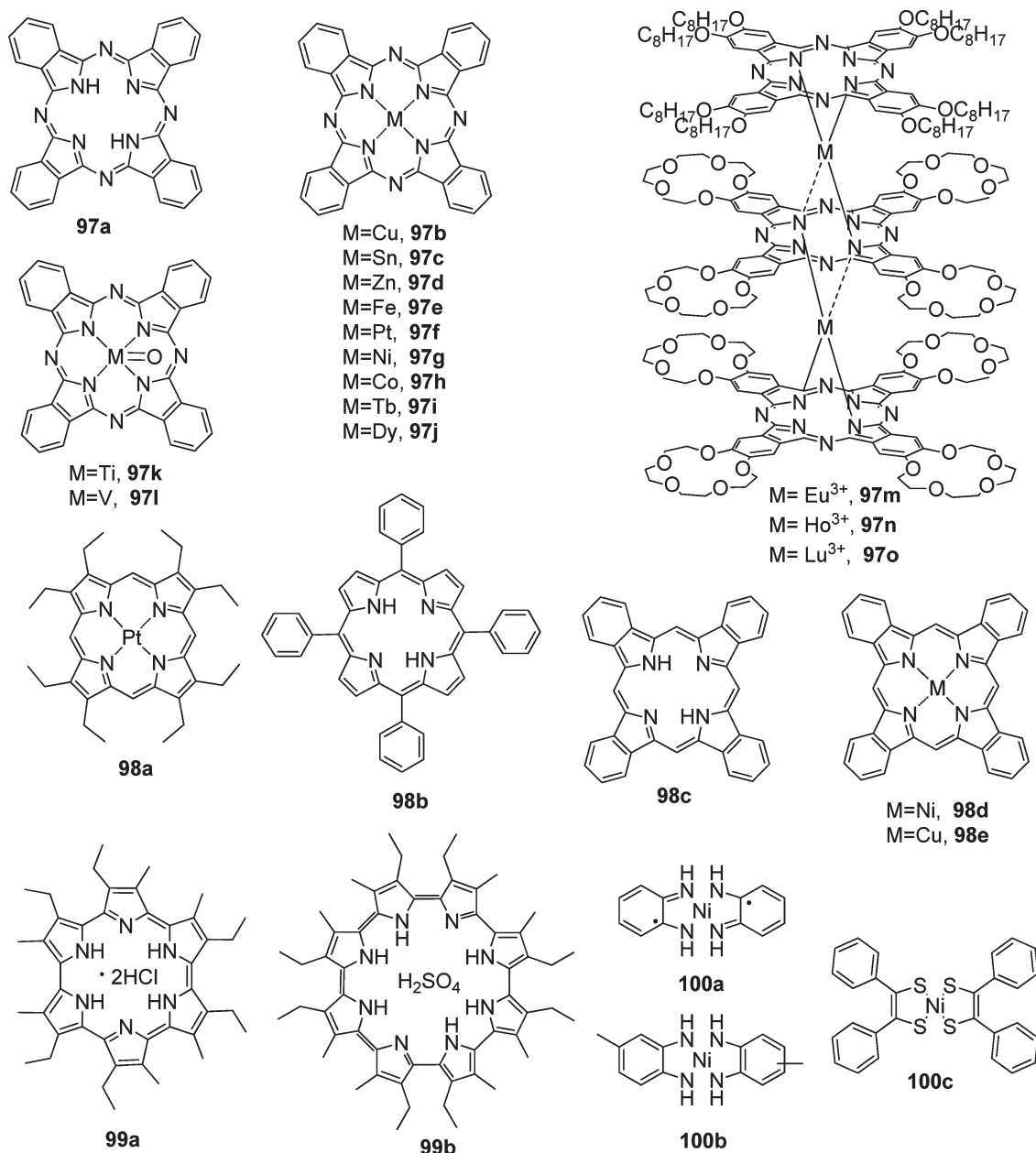


molecules of the phthalocyanine family. Of these, copper phthalocyanine is probably the first material among these nitrogen-containing heterocyclic semiconductors that was studied for use in OFETs. Highly ordered, evaporated thin films of CuPc³⁰² showed a hole mobility of $0.02 \text{ cm}^2/(\text{V}\cdot\text{s})$ and an on/off current ratio of 10^5 . The mobility of its single crystal transistors^{303,304} could even reach up to $1 \text{ cm}^2/(\text{V}\cdot\text{s})$. OFETs of phthalocyanine (**97a**) and ZnPc (**97d**)³⁰⁵ showed mobilities of $10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$. By using CuPc as the first active layer and cobalt phthalocyanine (CoPc, **97h**) deposited on it as the second active layer, sandwich configuration³⁰⁶ devices showed mobilities as high as $0.11 \text{ cm}^2/(\text{V}\cdot\text{s})$, which was higher than that of CuPc or CoPc. Thin film transistors based on LnPc (Ln = Tb (**97i**), Dy (**97j**))³⁰⁷ showed a hole mobility of $10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s})$ for **97i** and ambipolar characteristics for **97j** with an electron mobility of $10^{-5} \text{ cm}^2/(\text{V}\cdot\text{s})$ and a hole mobility of $10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s})$.

Titanyl-phthalocyanine (**97k**, TiOPc) and vanadyl-phthalocyanine (**97l**, VOPc) are different from the planar metal phthalocyanines in

that they are nonplanar, polar molecules. The TiOPc evaporated films³⁰⁸ had four phases: amorphous phase, monoclinic phase I (β), triclinic phase II (α), and phase Y. The crystals of the α phase adopt a typical lamellar structure with a large π - π overlap and strong π - π intermolecular interactions. Thin film transistors based on the α phase showed a mobility of over $1 \text{ cm}^2/(\text{V}\cdot\text{s})$ and the highest mobility reached $10 \text{ cm}^2/(\text{V}\cdot\text{s})$.³⁰⁹ High quality VOPc films were obtained when deposited on thin ordered para-sexiphenyl (*p*-6P) layers with a high substrate temperature.^{310,311} Transistors based on these VOPc/*p*-6P films showed mobility of $1.5 \text{ cm}^2/(\text{V}\cdot\text{s})$. A concurrent work involving VOPc OFETs³¹² was performed by Hu's group, and a mobility of $1.0 \text{ cm}^2/(\text{V}\cdot\text{s})$ was obtained on ODTs-modified SiO₂/Si substrates. A class of amphiphilic tris-(phthalocyaninato) rare earth triple-decker complexes (**97m-o**)³¹³ were also reported. Using the Langmuir-Blodgett (LB) technique, these complexes adopted a face-on orientation on the substrates, and transistors based on these LB films exhibited high performance with mobilities as high as 0.6, 0.4, and $0.24 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively.

Chart 20. Phthalocyanines, Porphyrins, and Organometallic Complexes

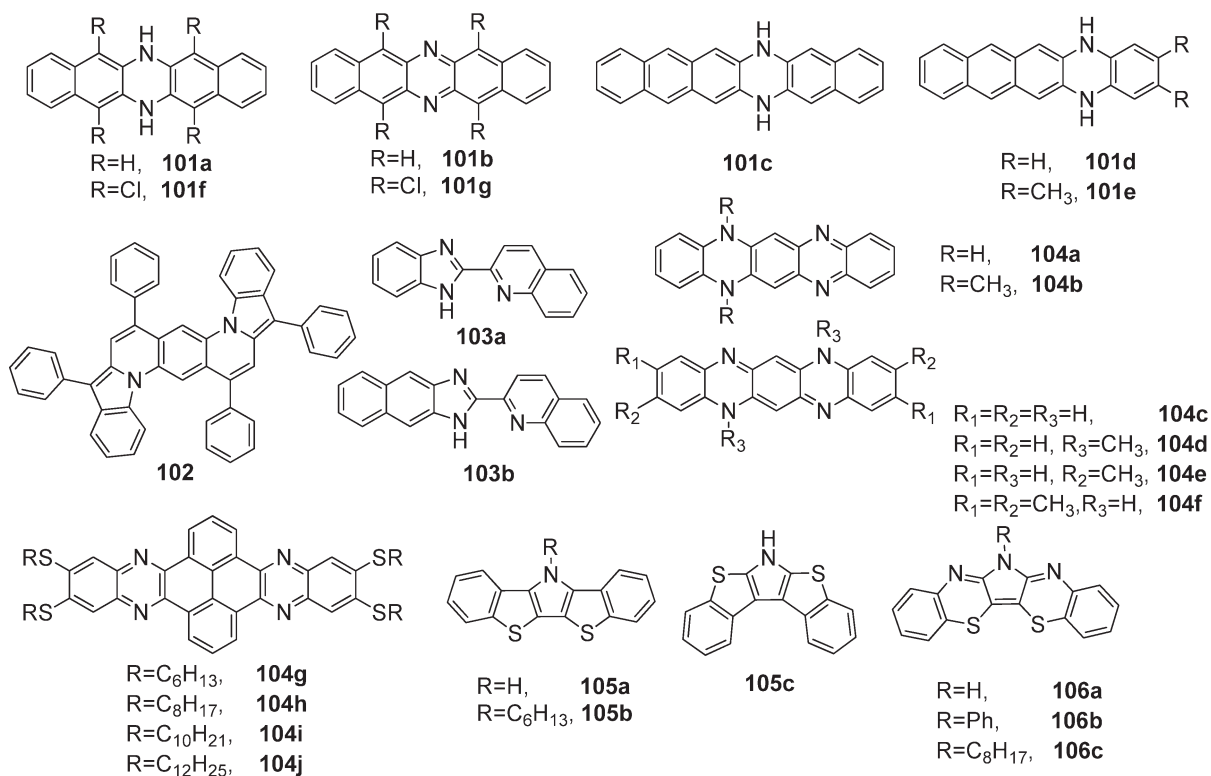


Similar to phthalocyanine, porphyrin derivatives³¹⁴ were also applied in OFETs. Octaethyl porphyrin platinum(II) (**98a**)³¹⁵ films grown by thermal evaporation on the (001) surface of KBr single crystals showed a mobility at 10^{-4} cm²/(V·s). Devices of the tetraphenyl porphyrin (**98b**)³¹⁶ and tetrabenzoporphyrin (**98c**)³¹⁷ exhibited improved field-effect performance with mobilities at 0.012 cm²/(V·s) and 0.017 cm²/(V·s), respectively. The spin-coated films of nickel (**98d**)³¹⁸ and copper (**98e**)³¹⁹ tetrabenzoporphyrin demonstrated mobilities of up to 0.2 and 0.1 cm²/(V·s), respectively. Analogous extended porphyrin compounds cyclo[6]pyrrole (**99a**)³²⁰ and cyclo[8]pyrrole (**99b**)³²¹ were also examined in transistors. These molecules adopted a nearly coplanar conformation, and the extended π systems facilitate the formation of radical cations (which lower the reorganization energy). LB films of cyclo[8]pyrrole showed high

performance with mobility as high as 0.68 cm²/(V·s). In addition to the metal phthalocyanines and porphyrins, the electronic characteristics of some other metallo-organic complexes were also studied. Noro et al. reported that thin film transistors of bis(*o*-diiminobenzosemiquinonate) nickel(II) complex (**100a**)³²² showed mobility at 0.038 cm²/(V·s). Another two nickel coordination compounds (**100b,c**)³²³ reported by Mori's group, showed that **100b** exhibited typical p-channel performance with a mobility up to 0.013 cm²/(V·s), while **100c** displayed n-type behavior with an electron mobility of 10^{-5} cm²/(V·s).

3.1.3.2. Azaacenes. In addition to thiophene rings, pyrrole, pyridine, and pyrazine were also used as heteroaromatic units in organic semiconductors. A class of dihydrodiazapentacene derivatives (**101**)³²⁴ were prepared by Nuckolls et al. Of these,

Chart 21. Azaacenes



101a and **101c** showed mobilities of about 5×10^{-5} and 5×10^{-4} $\text{cm}^2/(\text{V}\cdot\text{s})$, respectively, while **101d,e** gave a mobility of 10^{-3} $\text{cm}^2/(\text{V}\cdot\text{s})$. Three polymorphic forms³²⁵ were found in thin films of **101a** (DHDAP). After further purification and device optimization, a mobility of 0.45 $\text{cm}^2/(\text{V}\cdot\text{s})$ was achieved. Similar reports on pentacene have appeared.^{7,326} As mentioned above, halogen groups substituted in the peri-position of acene might lead to π - π stacking (**26d,e**). As expected, single crystals of the two tetrachlorodiazapentacene derivatives (**101f,g**)³²⁷ revealed that the molecules adopted a slipped π - π stacking, and a high mobility of 1.4 $\text{cm}^2/(\text{V}\cdot\text{s})$ was obtained from films of TCDAP (**101f**) deposited on n-nonyltrichlorosilane (NTS) monolayer-modified SiO₂/Si substrates using a thin film of pentacene as the buffer layer. But the mobility of TCDAP (**101g**) was observed to be only 0.13 $\text{cm}^2/(\text{V}\cdot\text{s})$, which was much lower than that of **101f**. Single crystals of tetraphenylbisdoloquinoline (TPBIQ, **102**)³²⁸ exhibited a lamellar structure with 1D π - π stacking as shown in Figure 3C, and its OFETs showed mobility as high as 1.0 $\text{cm}^2/(\text{V}\cdot\text{s})$. The imidazolylquinoline derivatives (**103**) also showed p-type characteristics, and **103a**³²⁹ and **103b**³³⁰ gave mobilities of 0.038 and 0.148 $\text{cm}^2/(\text{V}\cdot\text{s})$, respectively. Liu's group synthesized a series of tetraazapentacenes derivatives (**104c, 104e,f**).³³¹ The amorphous films of **104c** and **104e** exhibited mobilities of 0.02 and 0.01 $\text{cm}^2/(\text{V}\cdot\text{s})$, respectively, while the tetramethyl substituted derivatives (**104f**) provided a much lower mobility of 10^{-5} $\text{cm}^2/(\text{V}\cdot\text{s})$. Further studies³³² suggested that the structure of DHTAP might be the benzenoid (**104a**) structure rather than the quinonoid structure (**104c**), and when DHTAP was methylated³³³ both benzenoid (**104b**) and quinonoid (**104d**) heteropentacenes were obtained.

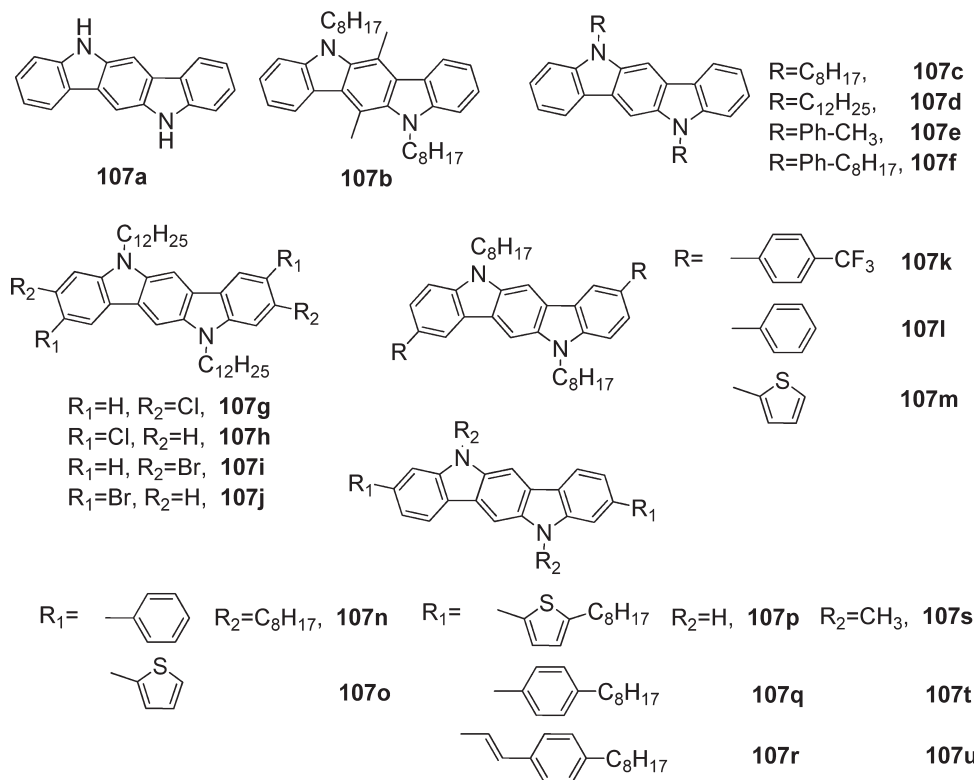
A series of novel pyrene discotics (**104g-j**)³³⁴ were synthesized and examined in OFETs. Transistors based on spin-coated

films of TQPP-[SC₁₂H₂₅]₄ (**104j**) showed typical p-type performance with an average mobility of 10^{-3} $\text{cm}^2/(\text{V}\cdot\text{s})$. Dibenzothieno[*b,d*]pyrrole (**105**)³³⁵ derivatives were developed by Liu's group. OFET mobility evaluated from the anti-isomer (**105a**) was 0.012 $\text{cm}^2/(\text{V}\cdot\text{s})$. However, no OFET characteristics were observed from the devices of **105b,c**. Zhu et al. synthesized a class of thiazine derivatives (**106**) which contained both sulfur and nitrogen atoms using a facile synthesis route. Transistors of **106a** exhibited typical p-type behaviors and mobilities of its thin film and single crystals were 0.34 ³³⁶ and 3.6 $\text{cm}^2/(\text{V}\cdot\text{s})$,³³⁷ respectively.

As mentioned above, substitution in the peri-position should facilitate π - π stacking. The derivatives of indolo[3,2-*b*]carbazole (**107b**)³³⁸ substituted at both N atoms and the middle benzene rings showed a lamellar arrangement in its single crystals. OFETs of **107b** films deposited on SiO₂/Si substrates showed p-channel behaviors with mobilities of about 10^{-3} $\text{cm}^2/(\text{V}\cdot\text{s})$ and an on/off ratio about 10^5 . A class of indolocarbazole derivatives (**107c-f**)^{339,340} substituted at the N atoms were synthesized by Ong et al. The vacuum deposited films of **107c** and **107d** provided mobilities in the range 10^{-3} - 10^{-4} $\text{cm}^2/(\text{V}\cdot\text{s})$. Films of **107e** showed rather low mobility (10^{-5} $\text{cm}^2/(\text{V}\cdot\text{s})$), but **107f** with a similar structure exhibited mobility at 0.12 $\text{cm}^2/(\text{V}\cdot\text{s})$, which was about 4 orders of magnitude higher than that of **107e**. Substitution at the *para* sites is expected to provide effective stabilization for hole injection, but substituents in the *meta* position are not expected to provide such effects. Ong et al. also developed a series of dihalo-substituted derivatives of the indolo[3,2-*b*]carbazoles (**107g-j**).³⁴⁰ The highest performance was obtained from **107h** with a mobility of 0.14 $\text{cm}^2/(\text{V}\cdot\text{s})$ and an on/off ratio at 10^7 .

Aryl groups functionalized at 2,8- or 3,9-positions of the indolo[3,2-*b*]carbazoles yielded the derivatives **107i-o**.³⁴¹

Chart 22. Indolocarbazole Derivatives



From **107l** to **107o**, the mobilities were found to be 0.06, 0.015, 0.2, and $0.03 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively. Tao's group has carried out thorough research on derivatives using aryl groups as substituents at the 2,8- or 3,9-positions of indolo[3,2-*b*]carbazole backbones. Single crystal transistors³⁴² of **107k** showed p-type characteristics with a mobility of $0.084 \text{ cm}^2/(\text{V}\cdot\text{s})$. Leclerc and co-workers found that except for **107r** and **107u**, the mobility of all the materials (**107p–u**)³⁴³ were all over $0.01 \text{ cm}^2/(\text{V}\cdot\text{s})$. The highest performance was obtained for **107q** with a mobility of $0.22 \text{ cm}^2/(\text{V}\cdot\text{s})$. Transistors based on indolo[3,2-*b*]carbazole (ICZ, **107a**) were fabricated later than its derivatives. The main reason was because the conventional methods for the synthesis of ICZ usually resulted in a mixture of isomers which were difficult to separate. Using proper solvents (DMF) for the growth of the crystals, single crystals of ICZ could eventually be obtained, and the vacuum deposited films of these crystals showed mobilities as high as $0.1 \text{ cm}^2/(\text{V}\cdot\text{s})$.³⁴⁴

3.1.3.3. Oligomers Based on Nitrogen-Containing π Systems. A series of carbazolenevinylene-based oligomers (**108a–h**)^{345,346} were synthesized by Leclerc's group. The highest mobility found was $0.3 \text{ cm}^2/(\text{V}\cdot\text{s})$, which was obtained for CPC (**108a**) with an on/off ratio up to 10^7 . Two cyclic carbazolenevinylene dimers (**108i–j**)³⁴⁷ were developed by Zhu's group. The cyclic conformation significantly improved the molecular arrangements in the solid state, with the result that both of them formed crystalline films (the linear dimer **108k**, on the other hand, gave only amorphous thin films). Additionally, because the cyclic conformation was able to reduce the reorganization energy a high OFET performance became possible. **108i** showed a mobility of $0.013 \text{ cm}^2/(\text{V}\cdot\text{s})$, and this was much higher than that of its corresponding linear dimer **108k**.

It is well-known that triphenylamine derivatives are widely used as hole-transport materials in electroluminescent devices

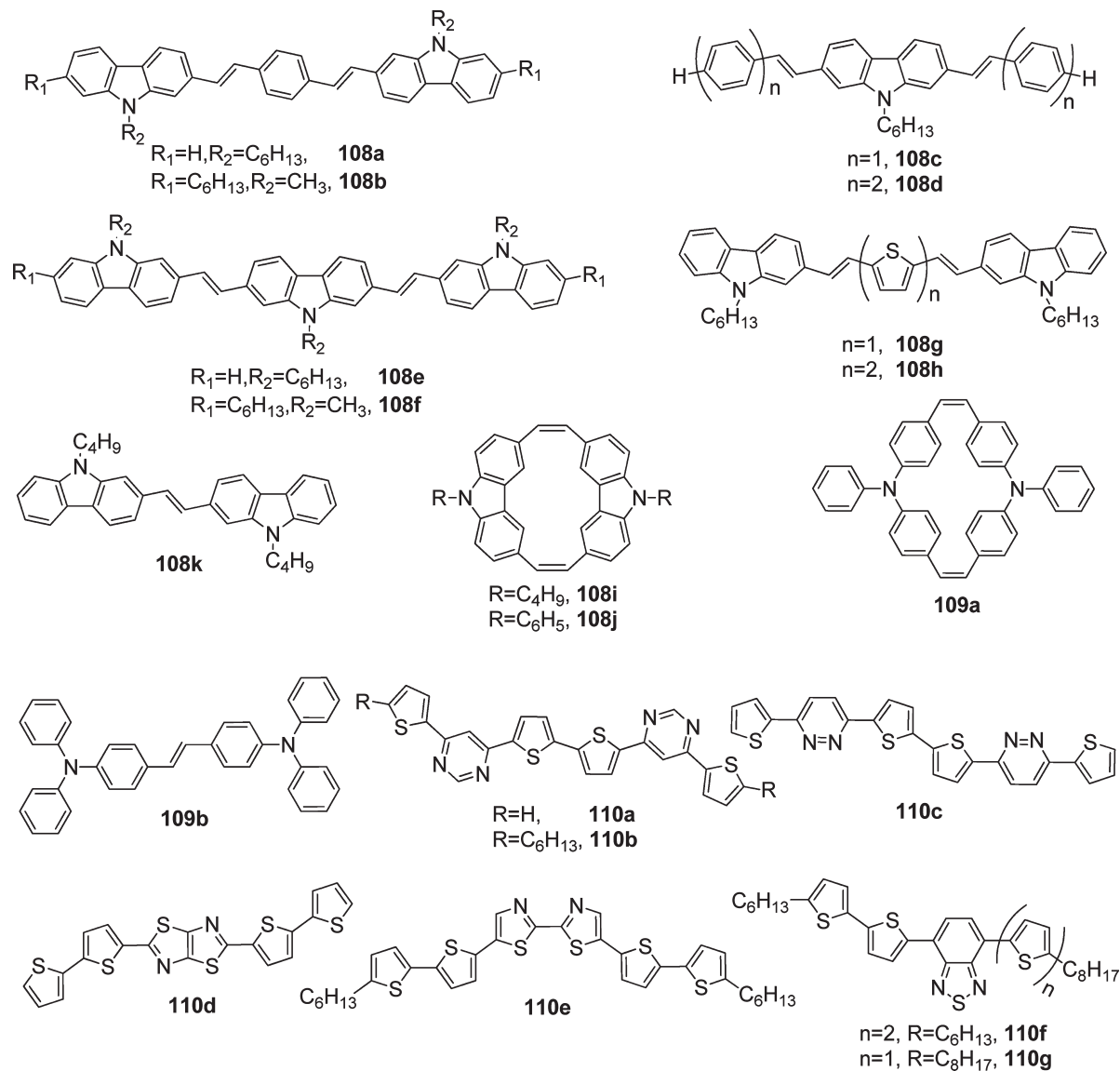
but rarely reported in field-effect transistors.^{235,348} This is because the nonplanar structure of these compounds results in the formation of amorphous films which are not beneficial for charge transport. In addition, OFETs based on triphenylamine derivatives³⁴⁹ usually showed low mobilities ($10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s})$). Recently, a cyclic triphenylamine dimer (**109a**)^{350,351} was developed by Zhu's group. It showed a rigid structure with ideal planarity, with the result that it favors the formation of crystalline thin-films and hence exhibited a field-effect mobility of $0.015 \text{ cm}^2/(\text{V}\cdot\text{s})$. This was two orders higher than that of its linear analogue (**109b**) ($10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s})$).

Donor–acceptor (D–A) materials are attractive for use in OFETs because the interactions between the HOMO of the electron-donating moiety and the LUMO of the electron-accepting moiety cause interesting electrical properties. Oligomers (**110a–c**)³⁵² containing thiophene and diazine showed p-channel transport with a rather low mobility ($10^{-3}–10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s})$). However, thiazole and thiazolothiazole derivatives^{101,353–356} gave much higher performance; for example, **110d** and **110e** gave mobilities of 0.02 and $0.011 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively. Also the benzothiazole-based oligomers^{357,358} **110f** and **110g** exhibited liquid crystalline behavior, and transistors based on their films showed mobilities of 0.17 and $0.02 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively.

3.2. N-Type Small Molecule Semiconductors

N-type semiconductors are essential materials for ambipolar transistors and complementary circuits.^{25,31} However, few semiconductors show high electron mobility and most n-type materials are unstable in air. An ideal n-type organic semiconductor requires that its LUMO energy level is close to the work function of the drain and source electrodes. This is so that electrons can easily inject from the source electrode into the organic semiconductor

Chart 23. Carbazole Derivatives and Other Nitrogen-Containing Compounds



and flow out of the semiconductor to the drain electrode efficiently. However, most electrode materials such as those made using Au and Pt, etc. possess a high work function which facilitates the injection of holes from the source electrode into the HOMO of organic semiconductor rather than electrons into the LUMO of the organic semiconductor. On the other hand, although electrodes such as Al, Ca, and Mg with lower work functions are well matched with the LUMO level of the organic semiconductor, they are usually highly susceptible to oxygen and hence can form charge transfer complexes with semiconductors. In order to match the LUMO level of the organic semiconductors with high work functions (Au, Pt, etc.), the introduction of electron-withdrawing groups such as halogen, cyano, carbonyl, etc. into the semiconductors is an efficient way of lowering the LUMO levels.³⁵⁹ Additionally, electron-withdrawing groups can increase the electron affinity of the materials³⁶⁰ as well as the air stability of their anions. It has been reported³⁶¹ that n-type semiconductors with ambient-stability require electron affinities greater than 4 eV. We will now introduce n-type organic

semiconductors based on the presence of the electron-withdrawing groups of halogen, cyano, and carbonyl.

3.2.1. Halogen-Containing Semiconductors. Because of the strong electron-withdrawing effect of halogen atoms, their introduction into organic semiconductor molecules is an important strategy for the design of n-type semiconductors. Fluorine is one of the most widely used substituents for realizing n-type behaviors.³⁶² For example, although pentacene is a benchmark molecule for p-type semiconductors, perfluoropentacene (**111a**)³⁶³ in fact possesses n-type characteristics. Transistors based on evaporated thin films exhibited electron mobilities as high as $0.11 \text{ cm}^2/(\text{V}\cdot\text{s})$. For comparison, pentacene films deposited under the same conditions showed p-channel transport behavior with a hole mobility of up to $0.45 \text{ cm}^2/(\text{V}\cdot\text{s})$. Their comparable mobilities have made pentacene and perfluoropentacene suitable for the fabrication of ambipolar transistors and complementary circuits. Bilayer transistors based on 10 nm perfluoropentacene and 35 nm pentacene showed ambipolar transport characteristics with hole and electron mobilities of

0.52 and $0.022 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively. The pentacene/perfluoropentacene complementary inverter exhibited a sharp inversion of output signal with a voltage gain of 57. The tetrafluoro (**111b**), octafluoro (**111c**), and tetrachloro (**111d**) substituted **28d** derivatives^{364,365} were also synthesized and characterized. OFETs based on **111b–d** showed ambipolar behavior. The LUMO energy level of the hexafluoro HBC (**112**)³⁶⁶ was about 0.5 eV lower than that of HBC, although energy gaps exhibited no significant change. Transistors based on vacuum-sublimated **112** films showed electron mobilities of $0.016 \text{ cm}^2/(\text{V}\cdot\text{s})$ and a current on/off ratio of 10^4 . A series of perfluorometallophthalocyanines (**113a–e**)³⁶⁷ were also used in OFETs. They showed good air stability and n-channel performance. For example, a widely studied compound is copper hexadecafluorophthalocyanine (F_{16}CuPc , **113a**). It showed an electron mobility of $0.03 \text{ cm}^2/(\text{V}\cdot\text{s})$. Single crystalline nanoribbons³⁶⁸ of **113a** were obtained by Hu's group, and the transistors produced showed a mobility of 0.2 and $0.35 \text{ cm}^2/(\text{V}\cdot\text{s})$ by using SiO_2 ³⁶⁸ and air/vacuum³⁶⁹ as the dielectric layers, respectively. Other phthalocyanines with halogen atoms, such as $\text{Cl}_{16}\text{CuPc}$ (**113f**),³⁶⁵ have also been studied. This air stable n-type semiconductor showed an electron mobility of $0.11 \text{ cm}^2/(\text{V}\cdot\text{s})$. An axially dichlorinated MPc, phthalocyanato tin(IV) dichloride (SnCl_2Pc , **113g**)³⁷⁰ was also examined. It showed an electron mobility of $0.3 \text{ cm}^2/(\text{V}\cdot\text{s})$ with a current on/off ratio at 10^6 . The high performance of these n-type semiconductors can be attributed to their close π – π stacking between molecules.

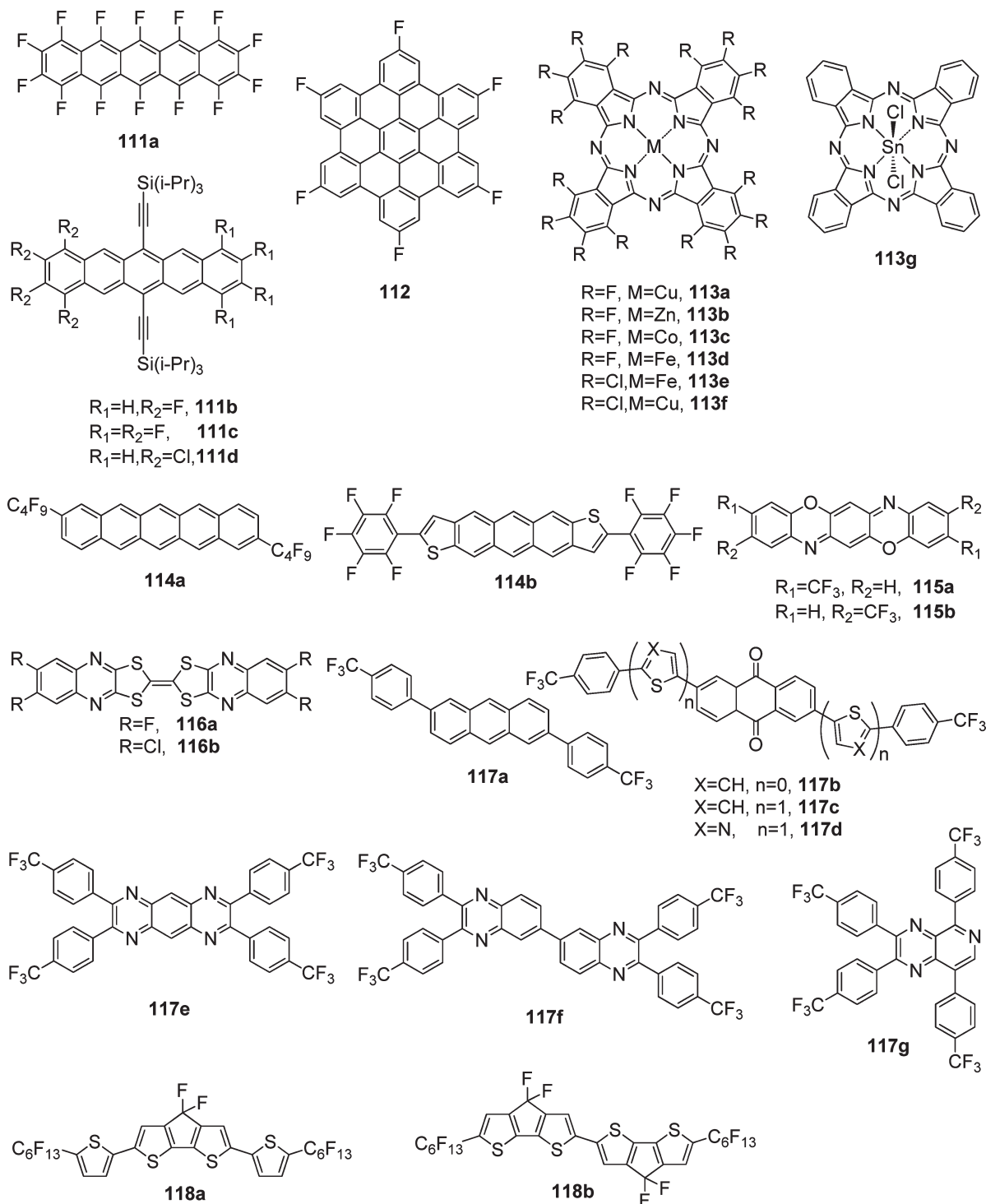
Many perfluoroalkyl and perfluorophenyl substituted derivatives were synthesized and examined in OFETs, and most of them exhibited n-type behaviors. For example, the perfluorobutyl substituted pentacene (**114a**)³⁷¹ showed an electron mobility of $1.7 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$ and the perfluorophenyl anthradithiophene (**114b**)¹⁶² exhibited ambipolar transport with an electron mobility of $6 \times 10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s})$ and a hole mobility of $0.05 \text{ cm}^2/(\text{V}\cdot\text{s})$. Yu and co-workers³⁷² reported two air stable trifluoromethyltriphenodioxazines (**115a,b**). Field-effect transistors based on them showed typical n-channel behavior with mobilities of 0.07 and $0.03 \text{ cm}^2/(\text{V}\cdot\text{s})$ for **115a** and **115b**, respectively. No significant degradation was observed after storing in air for one month. Tetrahalogen derivatives²⁴⁸ also exhibited high n-channel performance with electron mobilities of 0.1 and $0.11 \text{ cm}^2/(\text{V}\cdot\text{s})$ for **116a** and **116b**, respectively. This might in fact be the first TTF derivatives used in n-type transistors. Yamashita et al. used 4-(trifluoromethyl)phenyl as the electron withdrawing group and obtained an anthracene derivative (**117a**),⁸⁷ which showed an electron mobility of $3.4 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$ and an on/off ratio of 10^4 . Recently, a series of related anthraquinone derivatives (**117b–d**)³⁷³ were synthesized and used as the active layers in OFETs. The highest performance was obtained from **117d** which exhibited a mobility as high as $0.18 \text{ cm}^2/(\text{V}\cdot\text{s})$. Using 4-(trifluoromethyl)phenyl as the electron withdrawing group, fused-ring pyrazine derivatives³⁷⁴ were turned into n-type behaviors and transistors based on **117e,f** showed electron mobilities of 0.03 and $0.01 \text{ cm}^2/(\text{V}\cdot\text{s})$ under a nitrogen atmosphere. The derivative (**118a**)³⁷⁵ based on difluoromethylene-bridged bithiophene showed an electron mobility of $0.018 \text{ cm}^2/(\text{V}\cdot\text{s})$.

The oligomers (**119a**)³⁷⁶ with trifluoromethyl as the end-capped groups produced electron mobilities as high as $0.18 \text{ cm}^2/(\text{V}\cdot\text{s})$, while the 4T-based oligomers (**119b**)³⁷⁷ gave a mobility of $0.025 \text{ cm}^2/(\text{V}\cdot\text{s})$. A series of perfluoroalkyl (**119c–j**)^{289,378–380} end-capped oligomers were also developed. Of these, **119d**,

119h, **119i**, and **119j** gave mobilities about $10^{-2} \text{ cm}^2/(\text{V}\cdot\text{s})$ (after further optimization of the deposition conditions, the mobility of **119h** increased to 0.22)³⁸¹. The oligothiophenes (**120a–e**)^{381,382} substituted by perfluoroalkyl groups in the peri-position (side position) of the backbones exhibited low electron mobilities (lower than $5 \times 10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s})$), but p-channel characteristics were observed. However, when the substituents were situated in the middle thiophene rings (**120f–g**), even lower mobilities were obtained (10^{-6} – $10^{-8} \text{ cm}^2/(\text{V}\cdot\text{s})$). A series of thiazole-based oligomers (**121**)³⁷⁷ with trifluoromethylphenyl groups were synthesized by Yamashita et al. Interestingly, the molecule **121a** adopted an almost planar geometry and formed a two-dimensional columnar structure (2D lamellar stacking). The large π – π overlap between neighboring molecules resulted in a very high FET performance with an electron mobility as high as $1.83 \text{ cm}^2/(\text{V}\cdot\text{s})$. To date, this is the highest value reported for halogen n-type semiconductors. Single crystals of **121b** had a herringbone packing, and transistors based on its vacuum-deposited films failed to show any FET performance, although π -stacking also existed here. The mobilities of **121c–e** were about 0.0028, 0.085, and $0.018 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively. The oligomers (**121f,g**)³⁷⁶ based on thiazolothiazole end-capped with trifluoromethylphenyl groups also showed high n-channel characteristics with mobility up to $0.3 \text{ cm}^2/(\text{V}\cdot\text{s})$ for **121f** and $0.18 \text{ cm}^2/(\text{V}\cdot\text{s})$ for **121g** (an improved mobility as high as $1.2 \text{ cm}^2/(\text{V}\cdot\text{s})$)³⁸³ was also reported). However, these materials had threshold voltages usually higher than 60 V. It was found that more thiazole rings (**121h,i**)³⁸⁴ could lower the LUMO energy levels and decrease the threshold voltages to around 20 V. **121h** showed a mobility as high as $0.64 \text{ cm}^2/(\text{V}\cdot\text{s})$, while the mobility of **121i** was only about $10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s})$. This indicates that the position of nitrogen in these compounds is also a key for optimizing the performance of OFETs. The dithiazolylbenzothiadiazole derivative (**121j**)³⁸⁵ exhibited high n-type performance with a mobility of $0.068 \text{ cm}^2/(\text{V}\cdot\text{s})$. In contrast, the analogue **121k**^{386,387} showed an electron mobility of $0.19 \text{ cm}^2/(\text{V}\cdot\text{s})$. The benzobis(thiadiazole) derivative (**121l**)³⁸⁸ showed an even higher mobility up to $0.77 \text{ cm}^2/(\text{V}\cdot\text{s})$ in air. A series of oligomers containing perfluorophenyl or perfluorophenylene (**122**)^{285,389–391} were synthesized by Marks et al. The highest performance of these perfluorophenyl end-capped derivatives was obtained from **122a** with an electron mobility as high as $0.5 \text{ cm}^2/(\text{V}\cdot\text{s})$. However, the oligomers containing perfluorophenylene (**122d,e**) showed weak p-type behaviors with a hole mobility of $0.01 \text{ cm}^2/(\text{V}\cdot\text{s})$ for **122d** and $10^{-5} \text{ cm}^2/(\text{V}\cdot\text{s})$ for **122e**. It is interesting to note that these results were similar to the derivatives of **120f,g** in which the perfluoroalkyl substituents are situated at the middle thiophenes.

Recently, two oligomers containing oxadiazole units (**123a,b**)³⁹² were developed by Katz's group. Most surprisingly, the derivatives **123a** end-capped with perfluorobutyl groups, showed high p-type characteristics with a hole mobility of $0.18 \text{ cm}^2/(\text{V}\cdot\text{s})$. This is in spite of the fact that both the oxadiazole units and perfluorobutyl groups are electron-withdrawing groups. They attributed their findings to the HOMO and LUMO energy levels (HOMO at -5.99 eV and LUMO at -3.56 eV) facilitating hole transport rather than electron transport. The other compound (**123b**) showed n-channel performance with an electron mobility of $10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$. In addition, the derivatives (**123c,d**) without oxadiazole units, both exhibited n-channel behaviors with mobilities of 0.027 and $0.063 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively.

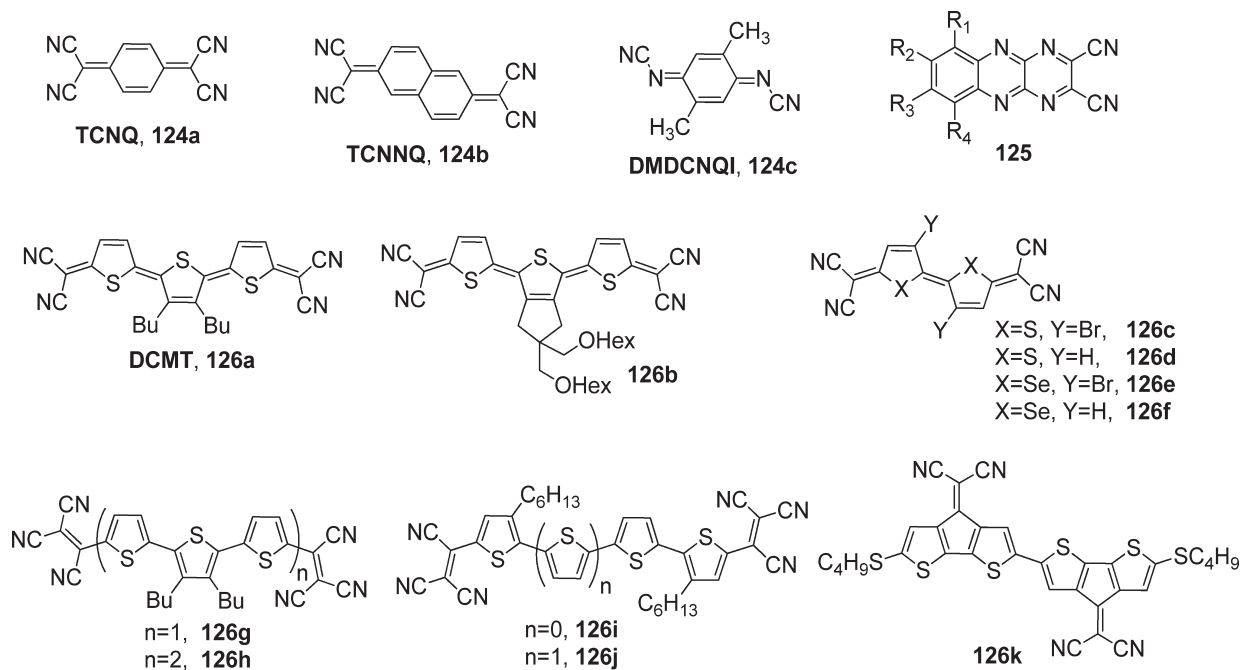
Chart 24. Halogen-Containing Acenes or Other Fused Ring n-Type Semiconductors



It is obvious that halogen atoms, especially fluorine atoms, due to their great electronegativity and small size (not expected to do harm to the packing motif), are one of the most widely used groups for the design of n-type organic semiconductors, because they work effectively to change the polarity of the organic semiconductors. As for the other electron-withdrawing groups described, fluorine atoms are usually used as coexistence groups in order to obtain organic semiconductors with high electron mobility and high environmental stability.

3.2.2. Cyano-Containing Semiconductors. N-type organic semiconductors containing cyano-groups are far fewer than those containing fluorine. TCNQ (**124a**), which is a representative example, is an electronic acceptor usually forming a charge transfer complex with TTF. In 1994, Brown et al.³⁹³ tested the transistor performance of TCNQ and showed that it exhibited n-channel behavior with an electron mobility of $10^{-5} \text{ cm}^2/(\text{V}\cdot\text{s})$. Using microcontact printing³⁹⁴ to pattern single crystal arrays of TCNQ, these single crystal devices exhibited a mobility about

Chart 26. Cyano-Containing n-Type Semiconductors



the acenes or heteroarenes have also been reported. The oligomer **126k**⁴⁰⁴ showed fascinating n-channel characteristics with an electron mobility of $0.34 \text{ cm}^2/(\text{V}\cdot\text{s})$. The use of cyano-groups in imides will be discussed in the next section.

3.2.3. Carbonyl-Containing Semiconductors and Imide Derivatives.

3.2.3.1. Carbonyl-Containing Semiconductors.

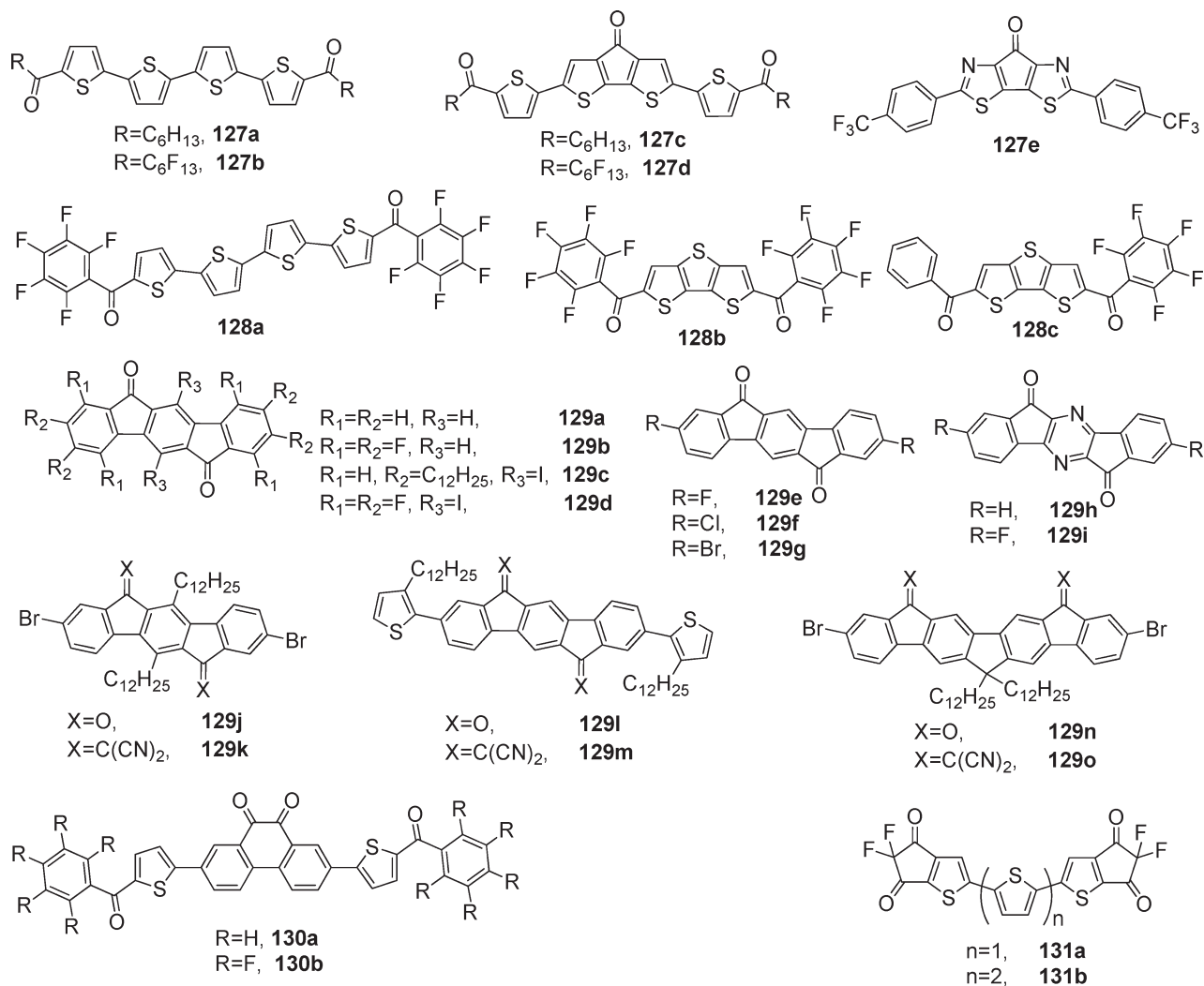
Carbonyl-containing semiconductors reported as being suitable for use in n-type transistors are most often combined with halogen or cyano-groups as the electron-withdrawing units. Facchetti and Marks et al. found that derivatives containing only carbonyl groups as the electron withdrawing groups (**127a**) on HMDS-modified SiO_2/Si substrates showed ambipolar properties with electron and hole mobilities of 0.1 and $0.01 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively.⁴⁰⁵ It was also found that the electron mobility could be further improved, up to $0.7 \text{ cm}^2/(\text{V}\cdot\text{s})$ on polystyrene (PS, 24 nm)/ SiO_2/Si substrates.⁴⁰⁶ In the case of the derivative **127c**, ambipolar activity⁴⁰⁷ was also detected. The derivatives of **127b** (DFHCO-4T), combined with C_6F_{13} groups, exhibited high n-type performance with electron mobility of up to $0.6 \text{ cm}^2/(\text{V}\cdot\text{s})$ and again these could be improved to $1.7 \text{ cm}^2/(\text{V}\cdot\text{s})$ on PS-(24 nm)/ SiO_2/Si substrates.⁴⁰⁶ These materials showed excellent stability in air. For example, **127d** (DFHCO-4TCO)^{405,408} with more electron-deficient groups operated well in air and exhibited no obvious degradation even after more than 20 cycles. Another carbonyl-bridged compound **127e**⁴⁰⁹ also showed an air-stable electron mobility up to $0.014 \text{ cm}^2/(\text{V}\cdot\text{s})$. Derivatives of **128**⁴¹⁰ with perfluorophenyl groups were also synthesized. Vacuum-deposited thin films of **128a** showed an electron mobility of up to $0.51 \text{ cm}^2/(\text{V}\cdot\text{s})$ and a mobility of $0.25 \text{ cm}^2/(\text{V}\cdot\text{s})$ for its drop-cast films. Transistors based on **128b** and **128c**²⁰⁴ exhibited low properties with mobilities of only 0.0015 and $0.03 \text{ cm}^2/(\text{V}\cdot\text{s})$. A series of antifuorenacenedione (**129a–d**)⁴¹¹ were prepared by Komatsu et al. Only the fluorinated derivative (**129d**) was reported as possessing n-type properties, but its mobility was rather low ($10^{-5} \text{ cm}^2/(\text{V}\cdot\text{s})$). Yamashita et al. synthesized a

series of antifuorenacenedione derivatives (**129e–i**).⁴¹² The difluorine derivatives (**129e**) showed good n-type FET behaviors. The highest mobility of $0.17 \text{ cm}^2/(\text{V}\cdot\text{s})$ and an on/off ratio of 10^7 were obtained from HMDS-treated substrates using bottom contact geometry. Under the same experimental conditions, **129f–i** showed mobilities of 1.8×10^{-2} , 9.9×10^{-3} , 2.7×10^{-4} , $1.1 \times 10^{-2} \text{ cm}^2/(\text{V}\cdot\text{s})$ (with an enhanced mobility of up to $0.17 \text{ cm}^2/(\text{V}\cdot\text{s})$ for a top contact device of **129i**), respectively. Another series of difunctionalized analogies (**129j–o**)^{413,414} were designed by Facchetti and co-workers. Here, the dicyanovinylene group-substituted derivatives (**129m**) showed n-type performance with electron mobilities as high as $0.16 \text{ cm}^2/(\text{V}\cdot\text{s})$ and on/off ratios in the range $10^7–10^8$. Moreover, no observable degradation was found after the devices were stored in air for 5 months.

Recently, two oligomers based on 9,10-phenanthrenequinone (**130**)⁴¹⁵ were designed and synthesized. The oligomer **130b** exhibited n-type activity with a mobility of $0.017 \text{ cm}^2/(\text{V}\cdot\text{s})$, while films of **130a** showed n-channel behavior with mobility at $10^{-5} \text{ cm}^2/(\text{V}\cdot\text{s})$ when the films were deposited on the substrate over 90°C . A series of compounds (**131**)⁴¹⁶ containing difluorodioxocyclopentene-annulated thiophene units were also synthesized. The **131a,b** films showed n-type characteristics with mobilities about 2.8×10^{-5} and $1.3 \times 10^{-2} \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively.

3.2.3.2. Imide Derivatives. Some of the diimides⁴¹⁷ that have been reported as active layers in n-channel organic field-effect transistors include pyromellitic diimides, naphthalene diimides, anthracene diimides, and perylene diimides. Naphthalene tetracarboxylic dianhydride (NTCDA, **132a**) is one of the first successes of this generation of n-type materials. It has been applied in the fields of field-effect transistors and organic heterostructures⁴¹⁸ since the 1990s. NTCDA films,^{419,420} deposited by vacuum sublimation, showed an electron mobility of $3 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$. The unsubstituted naphthalene diimides (NTCDI, **132b**) also

Chart 27. Carbonyl-Containing n-Type Semiconductors and Derivatives



showed n-channel properties with mobilities at about 10^{-4} $\text{cm}^2/(\text{V}\cdot\text{s})$. It was found that naphthalene diimides with alkyl substituents on the N atoms (**132c–h**)^{421–424} exhibited high electron mobility. For example, the octyl substituted derivative (**132d**) showed a mobility of $0.16 \text{ cm}^2/(\text{V}\cdot\text{s})$, and the sec-butyl (**132c**) and dodecyl functionalized derivatives (**132e**) showed mobilities of 0.04 and $0.01 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively.

Recently, Shukla et al.⁴²³ reported a cyclohexyl substituted naphthalene diimide (**132g**). Thin film transistors based on **132g** exhibited typical n-type performance with mobilities as high as $6.2 \text{ cm}^2/(\text{V}\cdot\text{s})$. In addition, the mobility was increased up to $7.5 \text{ cm}^2/(\text{V}\cdot\text{s})$ if the devices were measured in argon atmosphere under low humidity conditions. It is one of the highest values reported for n-type semiconductors so far. In contrast, the hexyl-substituted derivative (**132h**) showed a mobility of $0.7 \text{ cm}^2/(\text{V}\cdot\text{s})$, lower than that of **132g**. This behavior could be ascribed to their different molecular arrangements in the films, although they both showed lamellar motifs with strong $\pi-\pi$ intermolecular interactions (Figure 10). Where **132g** is concerned, every molecule interacts with four neighboring molecules through $\pi-\pi$ intermolecular interactions so that reticular charge transport is achieved. The $\pi-\pi$ intermolecular interactions are along

the *b* axis with extending interactions along the *a* axis. It gives 2D lamellar stacking (Figure 3D) which results in efficient charge transport and extremely high device performance. However, **132h** has $\pi-\pi$ interactions with only two neighboring molecules, so that column charge transport along the *a* axis is obtained (1D lamellar stacking (Figure 3C)), and less $\pi-\pi$ interactions all lead to much lower mobility.

When fluorine was introduced as a substituent, the materials exhibited n-type performance under ambient atmosphere conditions. For example, the derivatives of **132i–k**⁴²² showed electron mobility at $0.01 \text{ cm}^2/(\text{V}\cdot\text{s})$. The fluorinated derivatives (**132m**)⁴²⁵ showed similar mobility as **132l**. However, after being stored in air for 1 month, **132l** devices showed significant degradation, whereas no obvious degradation was found for **132m** devices. Recently, a series of fluorinated phenylethyl-substituted naphthalene diimides (**132o–q**)⁴²⁶ were synthesized by Katz et al. Films of **132n** and **132p** showed only low or even zero field effects. As for **132o**, in air the mobility reached $0.068 \text{ cm}^2/(\text{V}\cdot\text{s})$. The perfluorophenyl-substituted derivative (**132q**) gave a mobility as high as $0.31 \text{ cm}^2/(\text{V}\cdot\text{s})$. Transparent and flexible n-channel OFETs based on **132q** were fabricated on ITO-coated plastic PET films with PMMA as the dielectric layer.

Chart 28. Naphthalene Tetracarboxylic Diimides

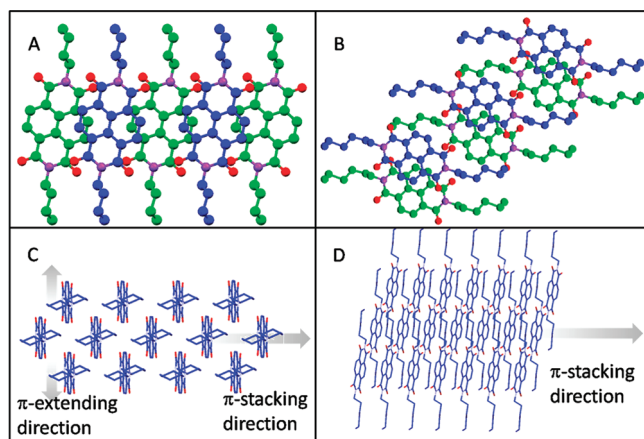
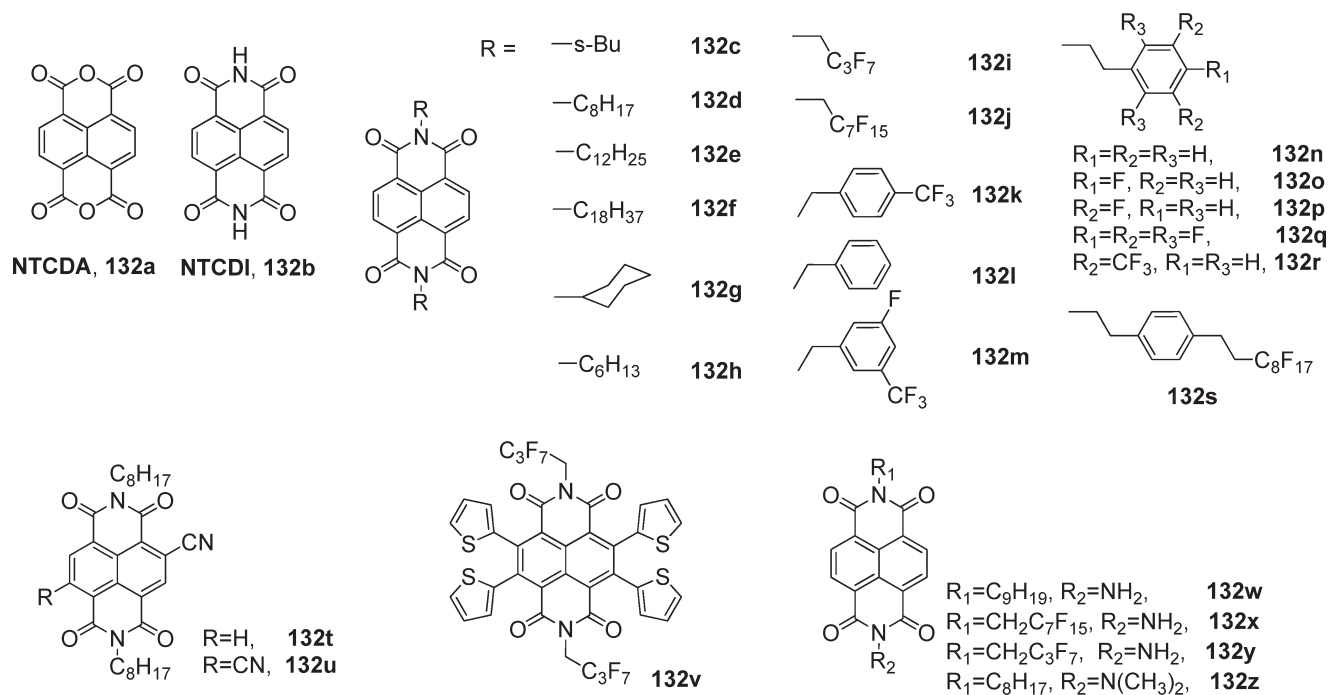


Figure 10. Top: overlap between neighboring molecules of (A) **132g** and (B) **132h**. Viewed perpendicular to the plane of the NDI core (blue: top layer, green: bottom layer). Bottom: crystal packing diagram of (C) **132g**, 2D π -stacking and (D) **132h**, 1D π -stacking. Protons are omitted for clarity. Crystallographic data for these compounds can be downloaded as Supporting Information for ref 423.

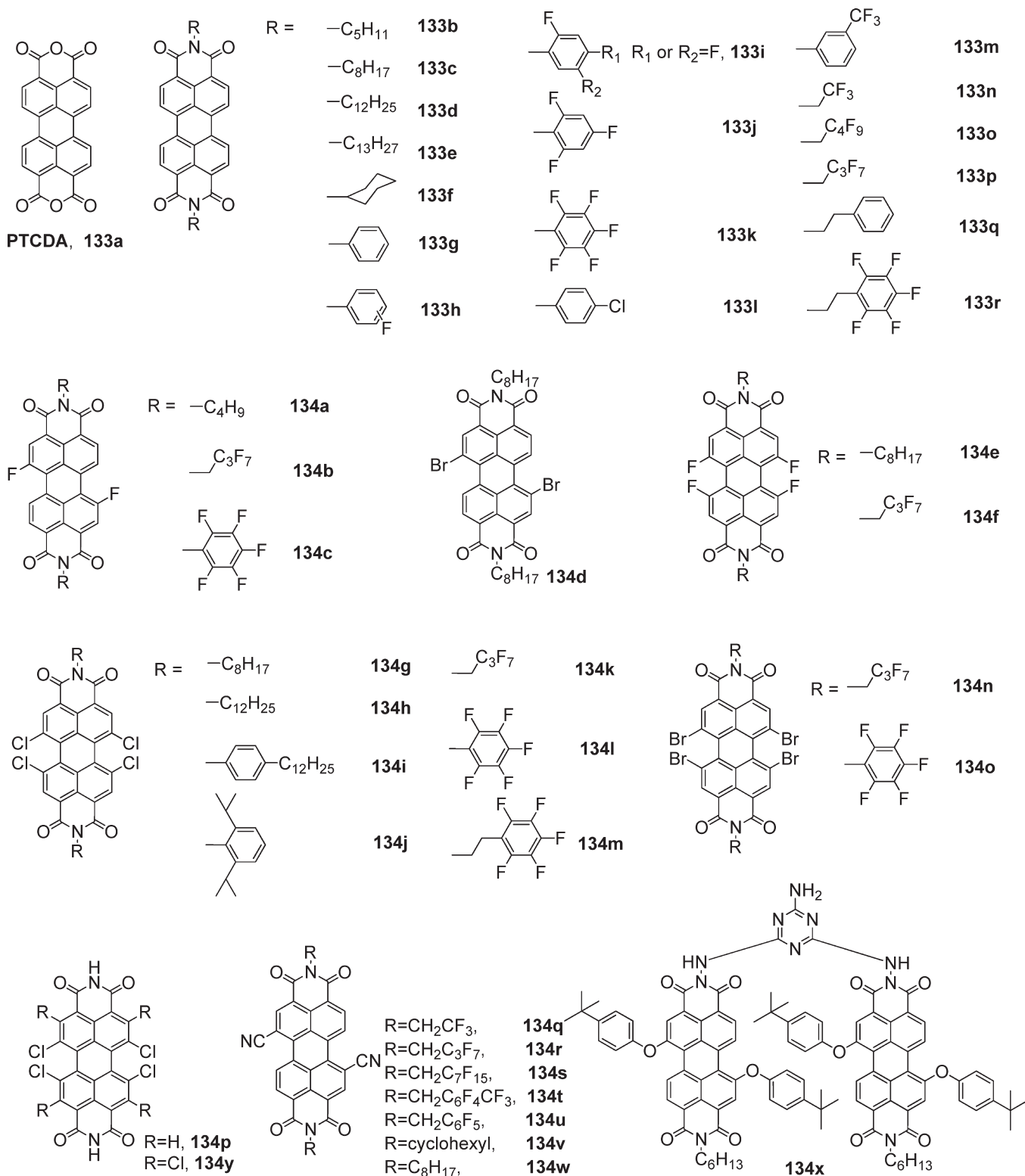
Typical devices exhibited mobilities at $0.23 \text{ cm}^2/(\text{V}\cdot\text{s})$. The compounds **132r,s**⁴²⁷ showed electron mobilities greater than $0.1 \text{ cm}^2/(\text{V}\cdot\text{s})$ in air, with **132s** reaching the highest at $0.57 \text{ cm}^2/(\text{V}\cdot\text{s})$.

Two cyanonaphthalene diimide semiconductors (**132t,u**)⁴²⁸ were synthesized with a view to improving the environmental stability of these semiconductors. The average electron mobility of NDI-8CN (**132t**) films was only at about $4.7 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$, while the mobility of NDI-8CN₂ (**132u**) was at $0.15 \text{ cm}^2/(\text{V}\cdot\text{s})$. Although the performance of **132u** was comparable to the derivatives (**132d**) which are unsubstituted by

ciano-groups, the mobility could be maintained as high as $0.11 \text{ cm}^2/(\text{V}\cdot\text{s})$ when tested under ambient atmosphere. It suggests excellent environmental stability of the compounds. The thiophene-substituted NDI derivatives (**132v**)⁴²⁹ (at 2,3,6- and 7-positions) exhibited only low transistor performance. The naphthalene diimides (**132x-z**)⁴³⁰ substituted by different length chains at the two nitrogen atoms were also prepared and examined in OFETs. However, a rather low electron mobility was obtained, and the highest value was only $3 \times 10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s})$ based on the films of **132x**.

With results similar to those for NTCDA, perylene tetracarboxylic dianhydride (PTCDA, **133a**) exhibited n-type charge transport properties⁴³¹ with an electron mobility of $10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s})$ under both vacuum or dehydration conditions. In addition, single crystal transistors⁴³² of PTCDA showed a mobility of $5 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$, which was 1 order of magnitude higher than that for its thin film devices under a vacuum. Using polycrystalline films of the octyl-substituted derivative (**133c**) as the semiconducting layer, a mobility^{433,434} as high as $1.7 \text{ cm}^2/(\text{V}\cdot\text{s})$ was obtained. In other results, the pentyl (**133b**)⁴³⁵ and dodecyl (**133d**)⁴³⁴ substituted derivatives showed mobilities up to 0.1 and $0.52 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively. Similar to the results for PTCDA, the mobility and current on/off ratio of these alkylated PTCDIs did not show any obvious change when tested in dry oxygen. The tridecyl-substituted derivative (**133e**)^{436,437} showed mobility up to $0.58 \text{ cm}^2/(\text{V}\cdot\text{s})$, and this⁴³⁸ could be improved up to $2.1 \text{ cm}^2/(\text{V}\cdot\text{s})$ when the devices were annealed at $140 \text{ }^\circ\text{C}$. However, the cyclohexyl (**133f**)¹⁴⁷ and phenyl (DPP, **133g**)^{439,440} substituted derivatives exhibited lower values of only about 1.9×10^{-4} and $0.017 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively. Halogenated alkyl and aryl substituents were also introduced into PTCDI molecules in the nitrogen atom positions. A series of halophenyl substituted PTCDI derivatives (**133h-m**)⁴⁴⁰ were synthesized by Chen et al. The monofluoro-, monochloro-, and trifluoromethylphenyl-substituted

Chart 29. Perylene Tetracarboxylic Diimides



derivatives all showed low mobility in the range of 10^{-3} – 10^{-4} cm²/(V·s). The difluoro-, trifluoro-, and perfluorophenyl-substituted derivatives were usually over 10^{-2} cm²/(V·s), and the perfluorophenyl substituted compounds (DFPP, **133k**) had a mobility of 0.068 cm²/(V·s) with an on/off ratio of 10^5 .

With the introduction of the halogen groups, the stability and mobility of the materials both improved. For example, after storage in air for 72 days, device performance of **133k** exhibited no significant change, which suggests excellent environmental stability of this compound. The fluoroalkyl-substituted perylene

tetracarboxylic diimide (**133n–p**)^{441,442} showed mobility at about 0.049, 0.11, and 1.44 cm²/(V·s), respectively. Although the mobility decreased about 20% immediately after the device was exposed to air, it maintained this value even after 50 days. Highly ordered OTS-modified layers could be produced by a solution process which usually provided higher device performance than those from a vapor-processed OTS-modified layer. For instance, devices based on **133p** exhibited mobility as high as 1.42 cm²/(V·s) based on solution-processed substrates. This is much higher than that of the vapor-processed technique (0.72 cm²/(V·s)). The phenyl- (**133q**)⁴⁴³ and perfluorophenyl-ethyl (**133r**)⁴⁴² substituted compounds exhibited mobilities about 0.11 and 0.62 cm²/(V·s), respectively. OFETs⁴⁴⁴ based on individual wires of **133q** showed a mobility of 1.4 cm²/(V·s) and devices of thin films exhibited an average mobility of 0.24 cm²/(V·s).

Perylene diimides functionalized at the perylene cores have also been studied (**134a–o**)^{417,442,443,445,446} by Bao, Würthner, and Marks et al. The derivatives functionalized at the perylene cores by difluorine groups usually showed higher (at least comparable) mobilities to those only substituted at the nitrogen atoms. For example, the difluorinated derivative (**134b**) gave a mobility of up to 0.66 cm²/(V·s), which was a little lower than its counterpart (**133p**, 1.44 cm²/(V·s)). On the other hand, **134c** gave a mobility of 0.85 cm²/(V·s), which was much higher than that of **133k** (0.068 cm²/(V·s)). Moreover, the difluorinated derivative (**134a**) also showed a mobility as high as 0.74 cm²/(V·s). When all the bay positions were substituted, for example, tetrachlorinated and tetrabrominated derivatives, the results differed from those of the difluorinated derivative. Except for **134l** and **134p** which showed higher mobilities (0.38 and 0.18 cm²/(V·s)) than the derivatives unsubstituted at the perylene core (**133k**, 0.068 cm²/(V·s)), other tetrachlorinated and tetrabrominated derivatives (**134k**, **134m–o**) provided mobilities much lower than their counterparts with substituents only in the nitrogen positions. This is probably because of the nonplanar structures caused by too many substituents in the bay positions. Perylene diimides (**134q–w**) which were substituted by cyano-groups at their perylene cores were also synthesized and applied in OFETs and they proved also very stable in air. The evaporated films^{390,447–449} of core-cyanated derivatives **134r**, **134v**, and **134w** showed mobilities at 0.64, 0.1, and 0.16 cm²/(V·s), respectively. On the other hand, the other materials (**134q**, **134s**, **134t**, and **134u**)⁴⁴⁸ gave rather low mobility. Recently, single crystal transistors⁴⁵⁰ based on **134r** were fabricated, and they exhibited a mobility of 1–6 cm²/(V·s) under a vacuum and 0.8–3 cm²/(V·s) in air. Spin-coated films⁴⁵¹ showed electron mobilities around 0.15 cm²/(V·s) under a vacuum. The amphiphilic perylenetetracarboxyl diimide dimer (**134x**)⁴⁵² was found to form highly ordered films using LB techniques, and the resulting (21 layer) film transistors showed typical p-type behaviors with a mobility of 0.05 cm²/(V·s). Very recently, Cl₈-PTCDI (**134y**)⁴⁵³ containing eight chlorine substituents at the perylene core was reported by Bao and Würthner et al. Although a highly twisted perylene backbone was observed in the crystal structure, its thin films still showed electron mobility as high as 0.91 cm²/(V·s) under a nitrogen atmosphere and 0.6 cm²/(V·s) in air. Moreover, the properties were almost unchanged even after exposure to air for 20 months.

The 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (**135a**, PTCBI)^{454,455} is usually used as an electron acceptor in organic photovoltaic (OPV) cells. Using ODTs-modified substrates,

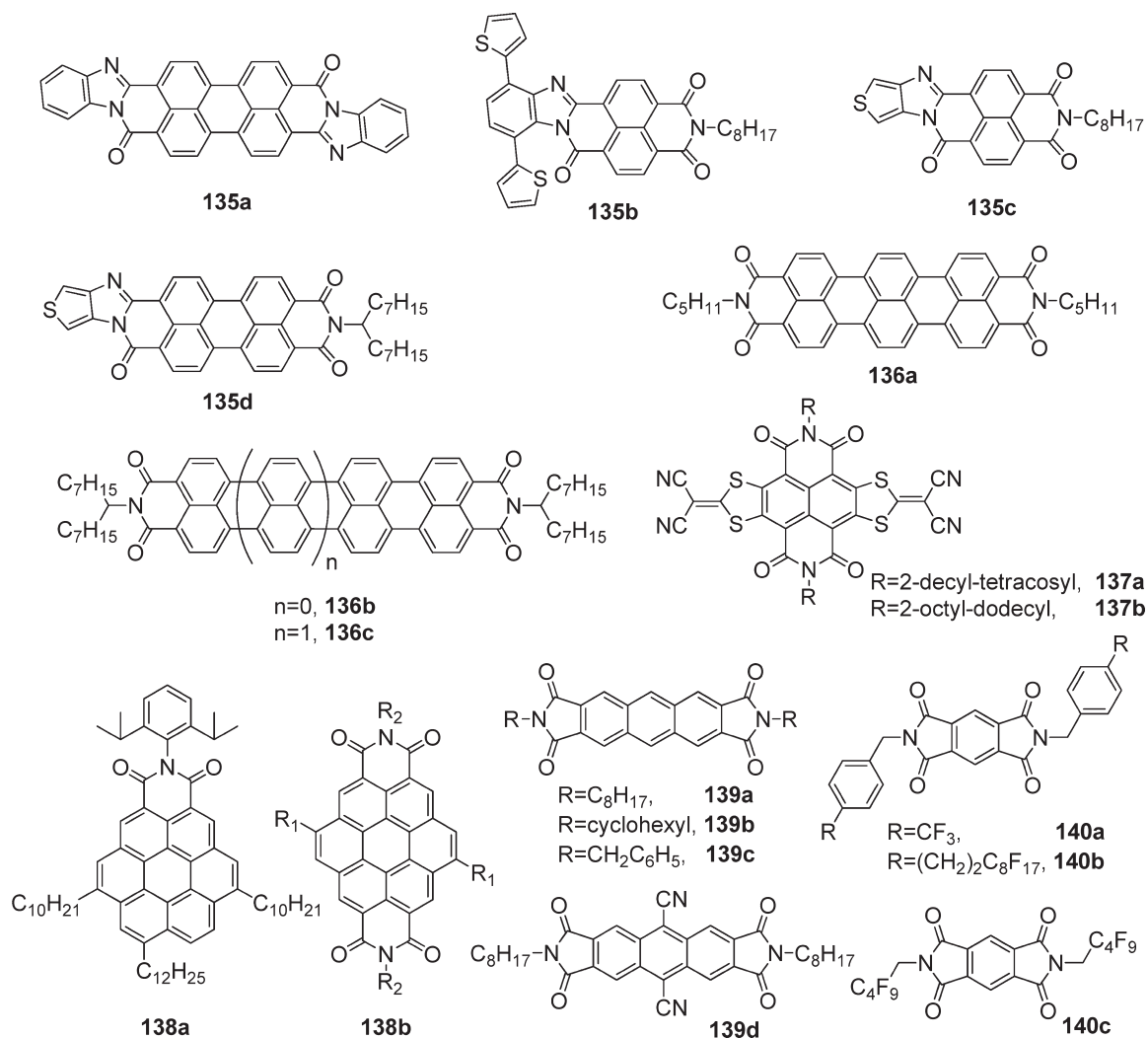
PCTBI films⁴⁵⁶ with a preferred orientation were obtained. The highly ordered ODTs self-assembled monolayer enhanced the electron transport ability so that the mobility of PCTBI reached 0.05 cm²/(V·s). Recently, a series of arylenediimide-thiophene derivatives (**135b–d**)⁴⁵⁷ were designed and synthesized. The highest performance was obtained from **135c** with an electron mobility as high as 0.35 cm²/(V·s) (**135b** and **135d** displayed mobility up to 0.10 and 0.15 cm²/(V·s), respectively). Some other examples of diimides used in OFETs are based on vacuum-deposited films of TTCDI-5C (**136a**)^{458,459}. They exhibited mobilities of 7.24 × 10⁻² cm²/(V·s). TDI (**136b**)⁴⁶⁰ showed obvious n-type behavior using a bottom-gate device structure with benzocyclobutene as the gate dielectric and aluminum as the source and drain electrodes. Interestingly, ambipolar transport was observed in its top-gate device with Au as the source-drain electrodes. Drop-cast films of a swallow-tailed quaterrylene tetracarboxydiimide (SWQDI, **136c**)⁴⁶¹ showed ambipolar properties with electron and hole mobilities of 1.5 × 10⁻³ cm²/(V·s) and 1 × 10⁻³ cm²/(V·s), respectively. Two core-expanded NTCDI derivatives (**137**)⁴⁶² were reported recently by Gao et al. The expanded π -system facilitated π – π stacking and the rich electron-withdrawing groups (malonitrile) depressed the LUMO energy levels, so that for solution-processed devices (**137b**) under ambient conditions the electron mobility reached 0.51 cm²/(V·s). Using a pulse-radiolysis-time-resolved-microwave-conductivity (PR-TRMC) technique, a coronene imide derivative (**138a**)⁴⁶³ gave a mobility of 0.3 cm²/(V·s), and the discotic liquid-crystalline coronene diimides (**138b**)⁴⁶⁴ exhibited mobilities as high as 6.7 cm²/(V·s) as measured using the space-charge limited current (SCLC).

A series of anthracenedicarboximides (ADIs, **139a–c**)⁴⁶⁵ were synthesized by Facchetti and Marks et al. An electron mobility at 0.02 cm²/(V·s) and an on/off ratio at 10⁷ were obtained. Further studies on the cyanated ADIs (**139d**) suggested a mobility of 0.02 cm²/(V·s) when tested in air with an on/off ratio over 10⁷. When devices of **139d** were measured under a vacuum, a similar mobility was observed (0.03 cm²/(V·s)). A series of pyromellitic diimides (**140a–c**)⁴⁶⁶ which contained minimal cores as for n-channel semiconductors, showed a performance comparable to the ADIs. The maximum mobilities were about 0.074, 0.079, and 0.03 cm²/(V·s) for **140a**, **140b**, and **140c**, respectively, with on/off ratios in the range of 10⁴–10⁵.

In summary, imides are one of the most important classes of n-type semiconductors. Although tetracarboxylic dianhydride show low performance under a vacuum, when the dianhydride is transformed into a diimide through alkylation at the nitrogen atoms, high electron mobilities become available. If more electron-withdrawing groups, such as fluorine atoms or cyano-groups, are introduced into the molecular structures (on the nitrogen substituents or on the π -conjugated core of the relevant molecules) most compounds exhibited high performance in air. It should be noted that the derivatives additionally modified at the perylene bay positions by difluorine groups usually showed higher (at least comparable) mobility than those only substituted at the nitrogen atoms. However, in summary most of the tetrachlorinated and tetrabrominated derivatives exhibited much lower mobility than their counterparts, which is probably due to the nonplanar structures caused by too many substituents in the bay positions.

3.2.4. Fullerenes. Fullerene and its derivatives constitute some of the pioneering semiconductors used in OFETs. N-Channel characteristics were detected from a mixture⁴⁶⁷ of

Chart 30. Other Diimides

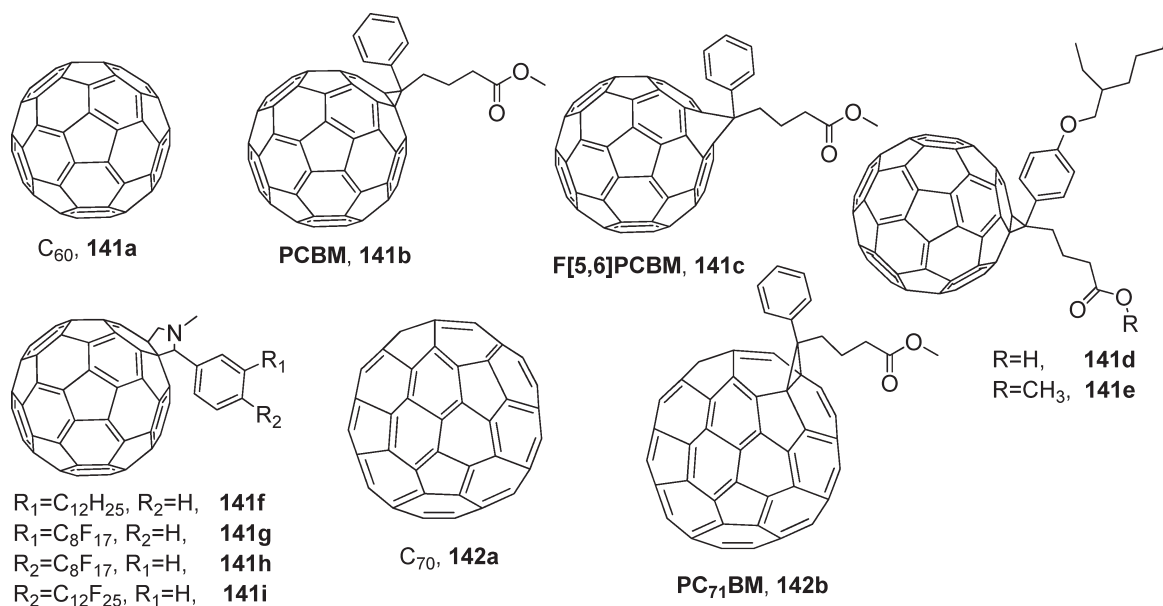


C_{60} (**141a**) and C_{70} (**142a**) field-effect transistors with an electron mobility of $5 \times 10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s})$. Using TOF measurements, C_{60} single crystals⁴⁶⁸ showed electron mobilities up to $0.5 \pm 0.2 \text{ cm}^2/(\text{V}\cdot\text{s})$ and hole mobility at $1.7 \pm 0.2 \text{ cm}^2/(\text{V}\cdot\text{s})$. In 1995, the first OFETs⁴⁶⁹ based on C_{60} were reported. Mobilities up to $0.08 \text{ cm}^2/(\text{V}\cdot\text{s})$ with on/off ratios of 10^6 in an ultrahigh vacuum were reported. When the substrates were treated with tetrakis(dimethylamino)ethylene (TDAE), due to the improved interface of C_{60} /substrate, the mobility was further increased to $0.3 \text{ cm}^2/(\text{V}\cdot\text{s})$. When alumina⁴⁷⁰ was used to cover C_{60} to shield the active layer from air, the mobility of the devices reached as high as $0.1 \text{ cm}^2/(\text{V}\cdot\text{s})$ and exhibited negligible degradation even after being stored in air for over a month. When C_{60} films were fabricated by molecular-beam deposition under ultrahigh vacuum (10^{-9} Torr), a mobility⁴⁷¹ of $0.56 \text{ cm}^2/(\text{V}\cdot\text{s})$ was obtained. Kitamura⁴⁷² realized low-operation voltage transistors of C_{60} -thin films by using a $\text{SiO}_2/\text{ZSO}/\text{SiO}_2$ (ZSO: the mixture of ZrO_2 and SiO_2) gate insulator. After the substrates were modified by ODTs, the mobility reached as high as $1.46 \text{ cm}^2/(\text{V}\cdot\text{s})$ with a threshold voltage as low as 1.9 V and an on/off ratio at 10^6 . A pentacene monolayer⁴⁷³ was used to improve the wettability of the substrates because of its strong tendency to form crystalline

films. After a pentacene buffer layer was introduced, the treated C_{60} devices gave electron mobilities up to $2.0\text{--}4.9 \text{ cm}^2/(\text{V}\cdot\text{s})$, as well as significant ambipolar operation. The highest mobility^{474–476} reached $6 \text{ cm}^2/(\text{V}\cdot\text{s})$ as a result of using a polymer as the dielectric layer. It was possible to attain $5.3 \text{ cm}^2/(\text{V}\cdot\text{s})$ ⁴⁷⁷ from crystalline film devices fabricated on octadecyltrimethoxysilane (OTMS) monolayer-treated SiO_2/Si substrates.

A soluble derivative of C_{60} , methanofullerene [6,6]-phenyl C_{61} -butyric acid methyl ester (PCBM, **141b**) was also developed and its performance was tested for use in OFETs. PCBM is usually used as an acceptor in organic photovoltaic cells, and its good charge transport properties qualified it as an ideal candidate for n-channel OFETs. Using Ca as the drain and source electrodes, spin-coated films⁴⁷⁸ showed a mobility of $4.5 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$. Anthopoulos et al.⁴⁷⁹ reported a p-n junction based on solution-processed PCBM films with an electron mobility of $0.01 \text{ cm}^2/(\text{V}\cdot\text{s})$ and a hole mobility of $8 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$. By judicious choice of polymers as dielectric materials, a mobility⁴⁸⁰ as high as $0.2 \text{ cm}^2/(\text{V}\cdot\text{s})$ was obtained from spin-coated films of PCBM. The related compound F[5,6]PCBM (**141c**) is methylated between the five-membered ring and its neighboring six-membered ring rather than between the two neighboring six-membered

Chart 31. Fullerenes



rings as in PCBM. However, transistors⁴⁸¹ using F[5,6]PCBM in the semiconducting layers exhibited mobility similar to that of PCBM. Both showed mobilities of $0.025 \text{ cm}^2/(\text{V}\cdot\text{s})$ by using high work function metal (Au) as the drain and source electrodes. When Ca was used in the electrodes, mobility was increased to $0.1 \text{ cm}^2/(\text{V}\cdot\text{s})$. Wudl's group⁴⁸² synthesized two [60]methanofullerene derivatives (**141d,e**), and their cast thin films gave mobilities of 1.59×10^{-3} and $1.04 \times 10^{-2} \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively. Solution-processed n-type OFETs based on C60MC12 (**141f**)⁴⁸³ have been reported by Chikamatsu et al. Spin-coated films showed mobility at $0.067 \text{ cm}^2/(\text{V}\cdot\text{s})$, while those of PCBM exhibited a mobility of about $0.023 \text{ cm}^2/(\text{V}\cdot\text{s})$. Unfortunately, devices based on these C_{60} derivatives showed poor stability with no activity in air. As mentioned above, the introduction of fluorine atoms would be expected to increase the mobility and improve the stability. A series of fluorinated C_{60} derivatives (**141g-i**)⁴⁸⁴ were synthesized by Chikamatsu et al. The perfluorododecyl substituted derivative (**141i**) displayed a mobility as high as $0.25 \text{ cm}^2/(\text{V}\cdot\text{s})$ in a vacuum and $0.078 \text{ cm}^2/(\text{V}\cdot\text{s})$ in air. The fluorinated derivatives of **141g,h** also exhibited good air stability.

OFETs based on the C_{70} fullerenes (**142a**)⁴⁸⁵ also showed n-type characteristics with mobility of $2 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$ but degraded rapidly when exposed to air. Soluble methanofullerene [6,6]-phenyl C_{71} -butyric acid methyl ester (PC₇₁BM, **142b**)⁴⁸⁶ was used as the semiconducting layer of OFETs, which exhibited a performance comparable to PCBM. The maximum mobility⁴⁸⁷ reached $0.21 \text{ cm}^2/(\text{V}\cdot\text{s})$ and $0.1 \text{ cm}^2/(\text{V}\cdot\text{s})$ for PCBM and PC₇₁BM, respectively. Other fullerenes such as C_{76} ,⁴⁸⁸ C_{82} ,⁴⁸⁹ C_{84} ,⁴⁹⁰ and C_{88} ⁴⁹¹ have also been examined recently, and mobilities were 3.9×10^{-4} , 1.9×10^{-3} , 2.1×10^{-3} , $2.5 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively.

4. POLYMER SEMICONDUCTORS

Polymer semiconductors are considered as one of the most appropriate candidates for OFETs due to their excellent electronic

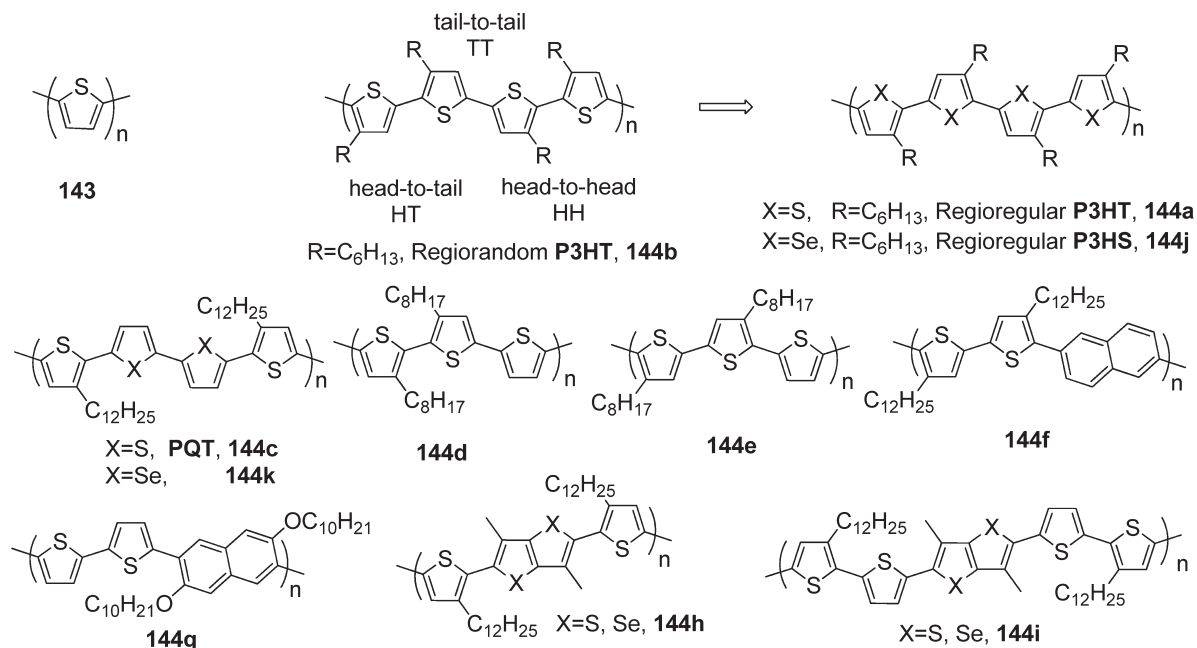
and optoelectronic properties. In addition, they have good solution-processabilities onto a range of desirable substrates such as other polymers. There are two kinds of charge transports in polymer transistors, namely, interchain transport ($\pi-\pi$ stacking orientation) and intrachain transport (Figure 4).^{42,492} The speed of intrachain transport is much faster than that of interchain. Additionally, polymers usually possess good flexibility, which renders them the most promising materials for large area flexible devices (such as flexible and folding integrated circuits, roll-up devices, electronic papers, etc.).

The first polymer field-effect transistors¹⁸ from polythiophenes were prepared using electrochemical methods. Films prepared by electrochemical polymerization showed both low quality and mobility. Through chemical modification, soluble polymers can be prepared in order to fabricate field-effect transistors using solution-processing techniques such as drop-casting, spin-coating, dip-coating, and ink-printing. However, because of their large molecular weights and complex chemical structures, it is usually difficult to arrange polymer molecules into the ordered structures regarded as highly essential for efficient charge transport. Using judicious synthetic methods,⁴⁹³⁻⁴⁹⁶ regioregular polymers were obtained with a head-to-tail (HT) regioregularity as high as 98–100%. Through controlling the deposition and self-assembly process, ordered molecular packing structures were also achieved in polymer films. However, the stability of these polymers decreased when alkyl groups were introduced into the molecular structures in order to improve their solubilities. Therefore, the discovery or invention of new conjugated units to create polymers with both high mobility and stability is highly imperative.

4.1. P-Type Polymer Semiconductors

The thiophene ring has become one of the most widely used building blocks for polymer field-effect transistors since the first polythiophene OFET was reported in the 1980s. The initial polythiophenes (**143**)^{18,497,498} used in FET were unsubstituted in the side positions. They were obtained by electrochemical

Chart 32. High Performance Polythiophenes



polymerization and showed low transistor performance with a mobility of 10^{-5} cm²/(V·s). In order to improve the quality of the films, different substituents were introduced into the side positions of the polythiophene backbones. Alkylated polythiophenes reported in early work (such as P3HT (**144b**))⁴⁹⁹ were regiorandom; the alkyl chains might have substituted in the 3- or 4-positions. In regiorandom P3HT, three kinds of random couplings exist: head-to-head (HH), tail-to-tail (TT), and head-to-tail (HT) coupling. The HH coupling causes a sterically twisted structure in the polymer backbone. This decreases the regioregularity and the π -conjugated systems. Using suitable synthetic routes, regioregular P3HT (**144a**) was obtained with a HT regularity of up to 99%. Its field-effect performance was investigated and results showed that the regioregularity played an important role in the molecular arrangement and subsequent OFET behaviors. Regioregular P3HT^{492,500} could adopt two kinds of arrangements on substrates, face-on and edge-on orientations. In addition, it was found that the mobility of the films that adopted an edge-on orientation (mobilities were as high as 0.05–0.2 cm²/(V·s))^{492,501–504} were usually about 2 orders of magnitude higher than those of the face-on orientation. Regioregular poly(3-hexyl)selenophene (**144j**)⁵⁰⁵ was also reported with a mobility at 0.02–0.04 cm²/(V·s).

A particular focus of polymer field-effect transistor research is how to improve their stability. There are three approaches for approaching this target. One way is to decrease the alkyl chains because a decrease in alkyl chains should not only lower the HOMO energy levels but also induce a twist of the thiophenes to shorten the extended π -conjugation and achieve a balance between mobility and stability. Ong et al. developed a class of solution-processable regioregular polythiophenes PQT,⁵⁰⁶ in which only half of the thiophene rings were substituted by alkyl chains. The HOMO energy level of PQT was only 0.1 eV lower than that of P3HT, but the mobility of dodecyl substituted PQT (**144c**) reached 0.14 cm²/(V·s). Slight degradation was observed after storing its devices in air for one month. The

related selenophene-based copolymer (**144k**)⁵⁰⁷ exhibited a lower mobility of 0.02 cm²/(V·s). Although the decrease in alkyl chains was found to work effectively to increase polymer stability, unfortunately, this method also decreased the solubility and mobility of the materials.

The second strategy is to increase the torsion of the polythiophene backbones directly by introducing head-to-head (HH) coupling. But this approach usually results in lower mobilities (**144i** showed a mobility of 0.03–0.04 cm²/(V·s), while **144h** exhibited a mobility lower than 10^{-6} cm²/(V·s) because of the torsion caused by the side chains⁵⁰⁸). The results suggest that **144d–f**⁵⁰⁹ are more stable than P3HT because their HOMO energy levels were found to be 0.2, 0.6, 0.8 eV lower. The highest mobility was obtained for **144d** at around 0.03 cm²/(V·s). Spin-coated films of the dialkoxyl substituted derivative **144g**⁵¹⁰ showed a comparable mobility at 0.02 cm²/(V·s).

The third approach is to introduce large conjugated units with high ionization potential into the polymer backbone. As is well-known, electrons from the fused aromatic unit are delocalized along the whole polymer chain only with difficulty because of the larger resonance stabilization energy of the fused rings.⁵¹¹ This results in low HOMO energy and high stability of the polymer semiconductors. McCulloch and co-workers^{511–515} synthesized a series of copolymers based on thieno[3,2-*b*]thiophene and thiophene rings (PBTTT, **145a**). The HOMO energy levels of **145a** were 0.3 eV lower than those of P3HT. Transistors based on **145a** exhibited a mobility of 0.7 cm²/(V·s), whereas 1.0 cm²/(V·s) was found for the tetradecyl substituted polymers even using high work function metals such as Pt as the source and drain electrodes. Mobilities up to 1 cm²/(V·s) were obtained from the cetyl-substituted polymers⁵¹⁶ by using Au as the source and drain electrodes on tridecafluorooctyltrichlorosilane-treated SiO₂/Si substrates. The thieno[2,3-*b*]thiophene-based polymers (**145b**)⁵¹⁷ showed a maximum mobility at about 0.15 cm²/(V·s) for the decyl-substituted derivatives. The dithieno[3,2-*b*:2',3'-*d'*]thiophene-based (**145c**)⁵¹⁸

and tetrathienoacene-based (**145e**)⁵¹⁹ copolymers showed mobilities at 0.3 and 0.33 cm²/(V·s), respectively. The homopolymers or copolymers based on alkylated at thieno[2,3-*b*]thiophene cores usually showed lower HOMO energy levels than that of **145a**. This is probably due to the torsion of the thiophene rings of the cores.^{520,521} Thin film transistors of **145d** showed a comparable performance (0.25 cm²/(V·s)) to that of **145a**. McCulloch and co-workers⁵²² further synthesized a class of alkylated (substituted on the cores) thienothiophene-based copolymers (**145f–h**). The trithienoacene- and pentathienoacene-based copolymers exhibited mobilities of 10⁻³ cm²/(V·s) due to the interference of side chains, but the tetrathienoacene-based copolymer possessing side chains in opposite directions showed a higher mobility of 0.087 cm²/(V·s). He et al. ascribed this phenomenon to the influence of C₂ symmetry on device performance.⁵²³ The benzodithiophene-based homopolymers (**146a**)⁵²⁴ and copolymers (**146b**)⁵²⁵ exhibited mobilities of 0.012 and 0.15 cm²/(V·s), respectively. In addition, the syn-benzodithiophene based polymers (**146c,d**)⁵²⁶ exhibited improved OFET performance: **146c** and **146d** had mobilities of 0.027 and 0.5 cm²/(V·s), respectively. Recently, a series of naphthodithiophene (NDT) copolymers (**146f**)⁵²⁷ were reported. Interestingly, although the BTBT-based small molecules showed high performance in field-effect transistors, no OFET performance was observed for the BTBT-based polymers (**146e**). However, the NDT-based polymers (**146f**) provided a mobility as high as 0.54 cm²/(V·s). The indacenodithiophene (IDT) based copolymer (**146g**)⁵²⁸ displayed a mobility as high as 1.2 cm²/(V·s). This was attributed to its large-scale crystallization in thin films compared to **146h** which had an amorphous structure. Kowalewski et al. synthesized a series of thiophene-based polymers with thiazolothiazole (PTzQTs, **147a,b**).⁵²⁹ Although the thiazolothiazole unit was considered a potential building block for n-type semiconductors,^{376,384} PTzQTs failed to show n-type performance. The hexyl, dodecyl, and tetradecyl substituted polymers⁵³⁰ showed hole mobilities of 0.05, 0.23, and 0.3 cm²/(V·s), respectively. McCullough et al. reported a series of copolymers⁵³¹ based on *N*-alkyldithieno[3,2-*b*:2',3'-*d*]pyrroles (DTP) and thiophene units. The highest performance was obtained from **147c** with a maximum mobility of up to 0.21 cm²/(V·s). The thiazole-based copolymers (**147d**)⁵³² were expected to possess high stability because of their donor–acceptor systems. The C₈H₁₇ and C₁₂H₂₅ substituted polymer exhibited mobilities at 0.04 and 0.14 cm²/(V·s), respectively. Indeed, the devices were very stable and no obvious degradation was observed even after the devices were stored in air for 60 days.

Polymers using fluorene as the building block are widely studied, and the most promising polyfluorene is based on dioctyl-fluorene copolymerized with thiophene units F8T2 (**148a**).^{533,534} F8T2 showed higher stability than that of P3HT due to its higher ionization potential. Moreover, F8T2 possessed a thermotropic, nematic LC phase above 265 °C. After annealing to get the LC phase, Sirringhaus's group⁵³⁵ achieved ordered films with enhanced mobility of 0.01–0.02 cm²/(V·s). After treatment with a DTS monolayer,⁵³⁶ the spin-coated films showed mobilities of 0.01–0.02 cm²/(V·s). The fluorene- and selenophene-based copolymer F8Se2 (**148b**)⁵³⁷ showed an OFET performance similar to F8T2 with a mobility of 0.012 cm²/(V·s). The mobility of **148e**^{538,539} reached up to 0.03 cm²/(V·s), while the other copolymers based on fluorene^{540–544} provided much lower values, for example, only 1.1 × 10⁻³ cm²/(V·s) for **148c**⁵⁴⁵ and 8 × 10⁻⁵ cm²/(V·s) for

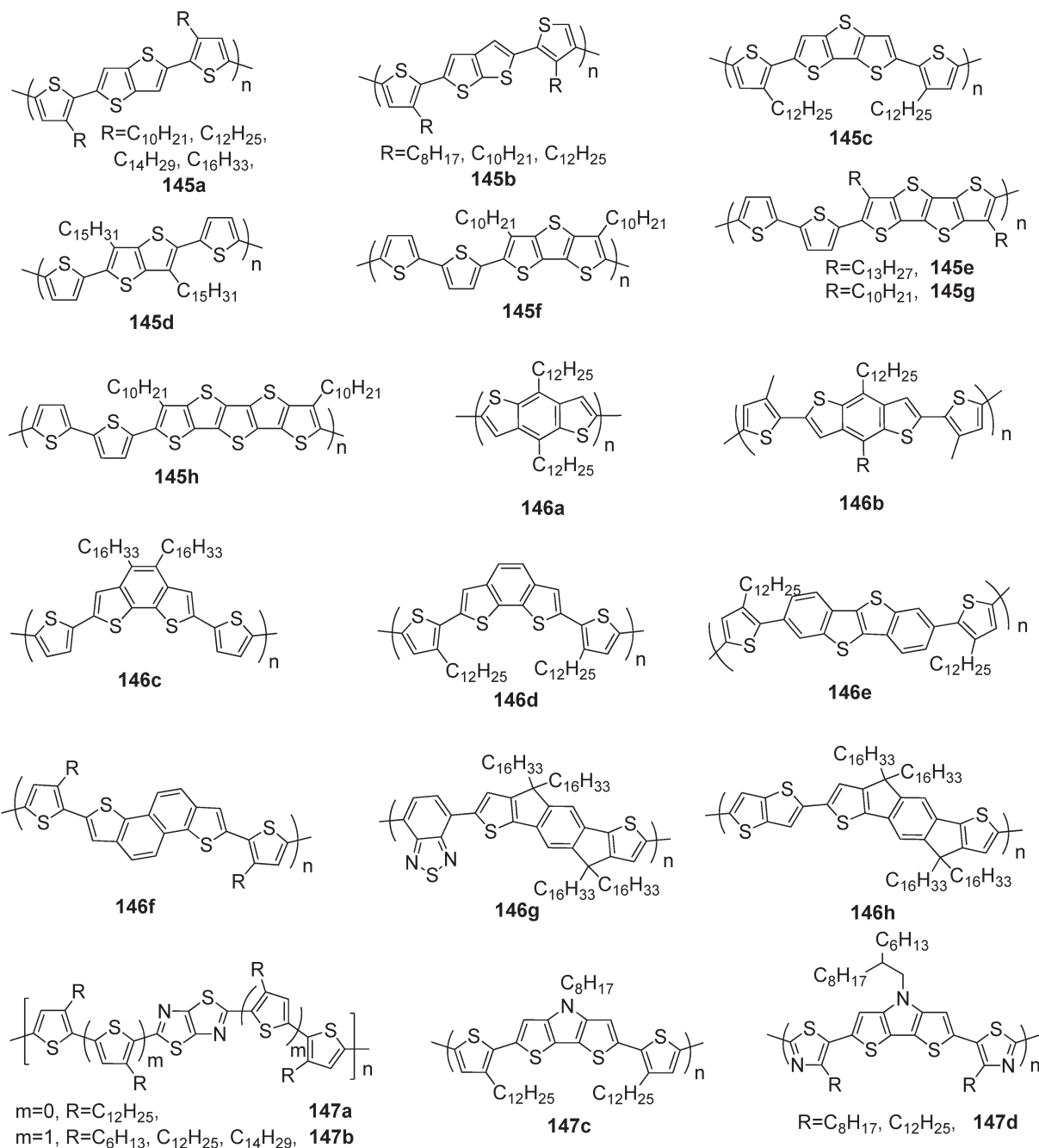
148f.⁵⁴³ Müllen's group⁵⁴⁶ developed a copolymer (**148g**) based on benzothiadiazole (BTZ) and cyclopentadithiophene (CDT). Films of **148g** drop-cast from a 1,2,4-trichlorobenzene solution gave a mobility of 0.17 cm²/(V·s) after annealing at 200 °C. After multiple purifications of BTZ and CDT before polymerization, high molecular weight polymers⁵⁴⁷ were obtained which produced a hole mobility up to 0.67 cm²/(V·s) for their spin-coated films. By using a dip-coating method, the macroscopic organization was further improved, resulting in hole mobilities at 1.0–1.4 cm²/(V·s) along the dip-coating direction and 0.5–0.9 cm²/(V·s) perpendicular to the dip-coated direction. A class of dibenzosilole-thiophene (**148i**) and dithienosilole-thiophene (**148h**) copolymers^{548,549} were synthesized by Facchetti and Marks et al. After annealing at 250 °C, **148h** gave a mobility of 0.08 cm²/(V·s) on HMDS-passivated SiO₂/Si substrates. The utilization of donor–acceptor architectures in the polymer backbones also proved an important strategy in the synthesis of π -conjugated polymers. Bao's group^{550,551} developed a series of D–A copolymers based on thienopyrazine (**148j–o**). These polymers showed mobilities as high as 0.2 cm²/(V·s) (for **148j**). In addition, the polymers also proved useful for the construction of organic photovoltaic cells with high efficiency. For example, when **148k** was used as the active layer it gave a power conversion efficiency up to 1.4%.

A series of D–A polymers (**149**)⁵⁵² were prepared by Wudl et al., and transistors based on **149a** and **149b** exhibited mobilities at 7.8 × 10⁻³ and 2.26 × 10⁻² cm²/(V·s), respectively. Polytriallamines (PTAA)^{553–555} constitute a class of polymer semiconductors with high stability. The devices based on **150a–c** showed excellent stabilities under ambient conditions with mobilities of 10⁻³–10⁻² cm²/(V·s). The highest performer **150c** measured around 0.04 cm²/(V·s). Although this mobility value is not particularly high, however, for amorphous films it proved outstanding. Polyindolo[3,2-*b*]carbazoles (**151a,b**)⁵⁵⁶ were developed by Ong's group. Interestingly, **151a** showed p-type performance with a mobility of 0.02 cm²/(V·s). No significant OFET performance was observed from thin-films of **151b**. Poly(*p*-phenylene vinylene) (**152a**, PPV)^{557,558} derivatives were also studied in OFETs with values around 10⁻³ cm²/(V·s). Hu and co-workers reported that thin-film transistors⁵⁵⁹ of poly(*para*-phenylene ethynylene) (**152b**, TA-PPE) showed a hole mobility around 4.3 × 10⁻³ cm²/(V·s). The transport characteristics of TA-PPE single crystal nanowires⁴⁰ exhibited mobilities up to 0.1 cm²/(V·s); several orders higher than that of its films. Structural analyses demonstrated that the backbones of the TA-PPE chains were parallel to the nanowire long axis with an edge-on motif, suggesting that efficient intrachain charge transport in the crystalline polymer nanowires is present.

4.2. N-Type Polymer Semiconductors

Reports on n-type polymer semiconductors are much rarer than those on p-type polymer semiconductors. Hence, the synthesis of n-type polymers is highly relevant and challenging for the development of polymer-based electronics. Ladder polymer BBL (**153a**)^{560–562} has an extremely high glass transition temperature (500 °C) and is insoluble in normal organic solvents. BBL films were prepared by spin-coating from Lewis acid/nitromethane solutions. Compared to its analogue BBB (**153b**), BBL showed a much higher performance with an electron mobility as high as 0.1 cm²/(V·s). This is several orders of magnitude higher than that of BBB (10⁻⁶ cm²/(V·s)).

Chart 33. High Performance Polythiophenes with Introduction of Large Conjugated Unit or Blocking Unit

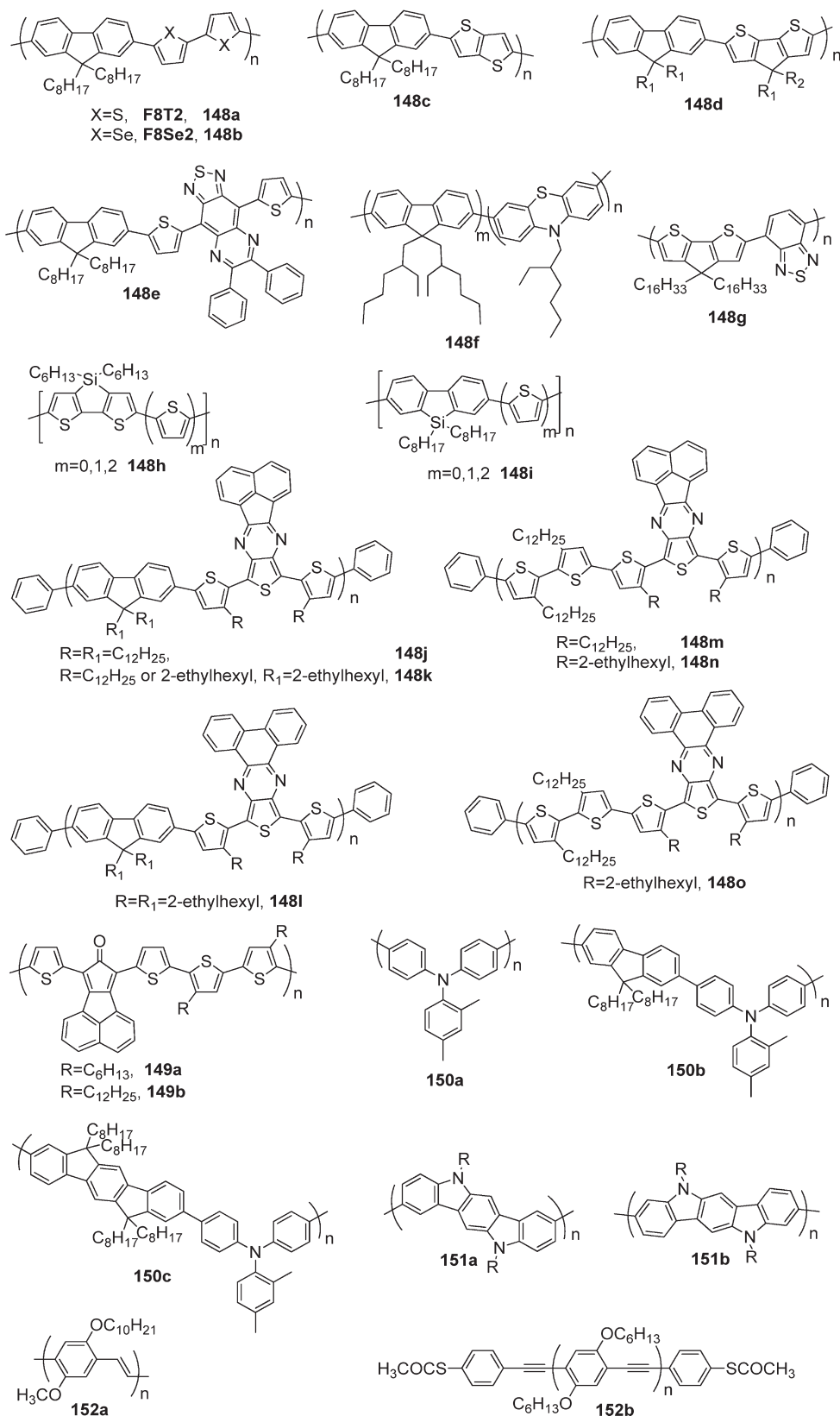


Although different from the cyclopentadithiophene-based copolymer **148g**, Donley et al. reported a fluorene-based copolymer F8BT (**154**)⁵⁶³ which showed n-type properties with an electron mobility of $4.8 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$. The spin-coated films of fluorophenacyl-quaterthiophene-based copolymer **155**⁴¹⁰ exhibited an electron mobility of $0.01 \text{ cm}^2/(\text{V}\cdot\text{s})$.

Zhan and co-workers synthesized a perylene diimide-thienodithiophene copolymer (**158a**),⁵⁶⁴ which displayed high n-channel behaviors with an electron mobility as high as $0.013 \text{ cm}^2/(\text{V}\cdot\text{s})$. Recently, Facchetti's group⁵⁶⁵ developed both a naphthalenedicarboximide- and a perylenedicarboximide-bithiophene based copolymer (**158b,c**). The results were very interesting.

The naphthalenedicarboximide-based copolymer (**158c**) showed high mobility ($0.06 \text{ cm}^2/(\text{V}\cdot\text{s})$) and good stability (with the mobility holding at $0.01 \text{ cm}^2/(\text{V}\cdot\text{s})$ after 14 weeks in air), whereas the perylenedicarboximide-based copolymer (**158b**) exhibited a lower mobility ($0.002 \text{ cm}^2/(\text{V}\cdot\text{s})$) and worse stability (the mobility decreased by 1 order of magnitude ($\sim 2 \times 10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s})$) within one week). An unprecedented OFET performance⁵⁶⁶ was obtained based on the naphthalenedicarboximide-based copolymer (**158c**) with an electron mobility as high as $0.45\text{--}0.85 \text{ cm}^2/(\text{V}\cdot\text{s})$ under ambient conditions. *N*-Alkyl-2,2'-bithiophene-3,3'-dicarboximide unit based homopolymer (**159a**) and copolymer (**159b**)⁵⁶⁷ were prepared. The homopolymer (**159a**) showed n-channel

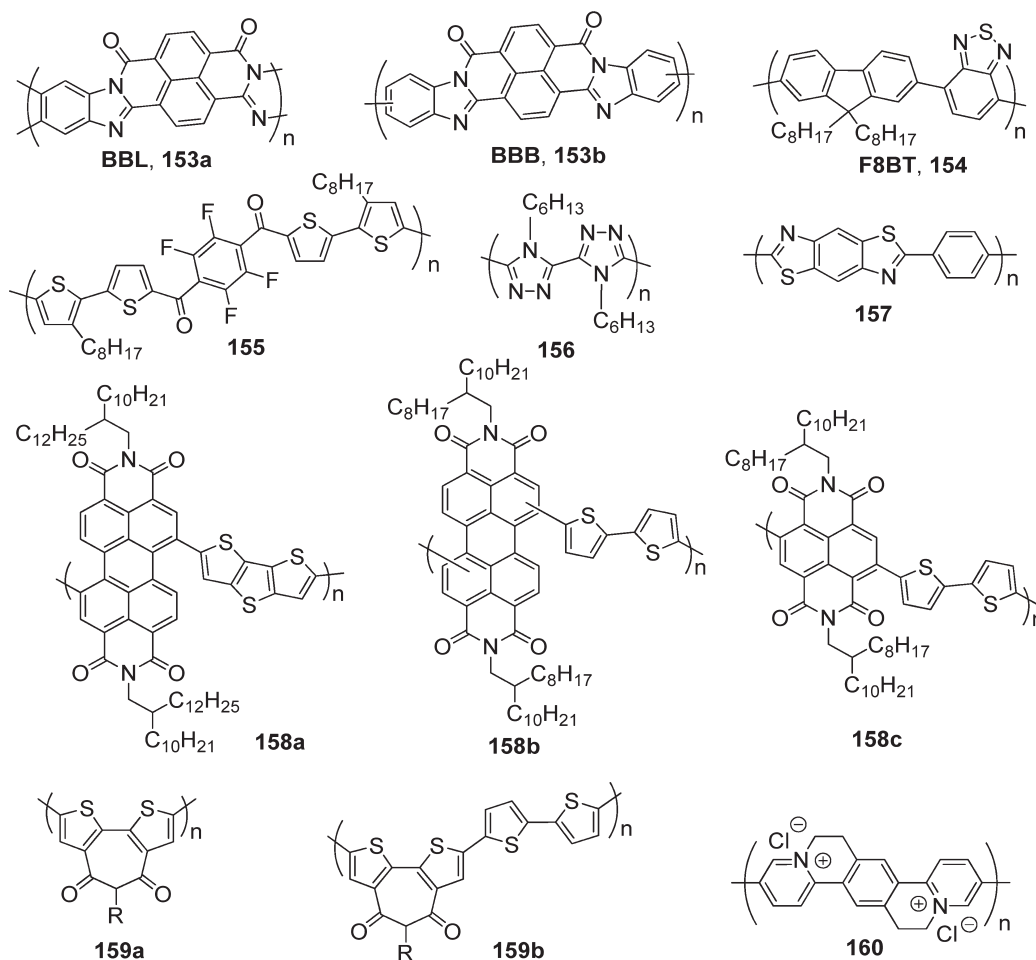
Chart 34. Some Other Typical p-Type Polymer Semiconductors



characteristics with an electron mobility of $0.01 \text{ cm}^2/(\text{V}\cdot\text{s})$, while the copolymer (**159b**) exhibited high p-channel

characteristics with a hole mobility of $0.01 \text{ cm}^2/(\text{V}\cdot\text{s})$. Interestingly, the water-soluble n-type poly(pyridinium phenylene)s

Chart 35. Representative n-Type Polymer Semiconductors



(160)⁵⁶⁸ were also reported for the first time with mobility up to $3.4 \text{ cm}^2/(\text{V}\cdot\text{s})$.

5. PROCESSING TECHNIQUES FOR OFETS

Because of their good flexibility, high solubility, and printability over a large area, OFETs have attracted particular attention for flexible displays and large scale integrated circuits among their many applications. Viewing the four types of OFET configurations (Figure 2), it can be seen that the bottom gate bottom contact (A) is highly convenient for the fabrication of devices because the semiconducting layer is the final one deposited after the electrodes and dielectric layer. However, the contact between electrodes and organic semiconductor in these devices is usually not as good as that found in top-contact devices (source/drain electrode on organic semiconducting layer). Therefore, bottom gate top contact devices (B) are widely utilized in the hope of getting better interfacial contact. Currently, bottom gate device configurations (A, B) are widely used for fundamental studies, while top gate modes (C and D) are more useful for practical applications.⁵⁶⁹

5.1. Techniques for Thin Film Transistors

Different techniques are available for the fabrication of organic thin film transistors.^{570,571} The most widely used method is vacuum deposition, which requires the semiconductors to remain stable around the sublimation point. By controlling the evaporation rate and the deposition temperature, continuous

films can be obtained with high mobility. For example, thin films of 18a (DPVAnt)⁵⁶ showed mobilities as high as $1.3 \text{ cm}^2/(\text{V}\cdot\text{s})$, only a little lower than its single crystals⁹¹ ($4.3 \text{ cm}^2/(\text{V}\cdot\text{s})$).

Over the past few years, many solution-processed techniques were developed for organic thin film transistors, such as LB techniques,³¹³ spin-coating,⁴⁶² dip-coating,⁵⁰³ drop-casting,⁵⁷² and zone-casting.²⁴¹ LB techniques can result in compact and ordered semiconducting layers. Dip-coating and zone-casting methods can provide films with high orientation. Thermal annealing at the temperature can further induce molecular self-assembly and hence improve device performance.⁵⁷³ Certainly, in order to obtain large scale integrated circuits of low cost, various kinds of printing techniques have been developed, with the result that organic electronics is also nicknamed “printed electronics”. For example, microcontact printing (Figure 11A)²¹ is an important printing technique that can eliminate thermal or solvent damage. Sirringhaus et al. used inkjet printing as shown in (Figure 11B)⁵⁶⁹ to fabricate OFETs. Sub-100 nm channel lengths were obtained with high resolution using this self-aligned inkjet printing technique.^{574,575} All layers (electrodes, semiconductors as well as dielectric layers) can be printed using an elastomeric stamp.⁵⁷⁶

5.2. Techniques for Single Crystal Transistors

Because of their perfect molecular arrangements, minimized defects, and eliminated grain boundaries in crystals, single crystal

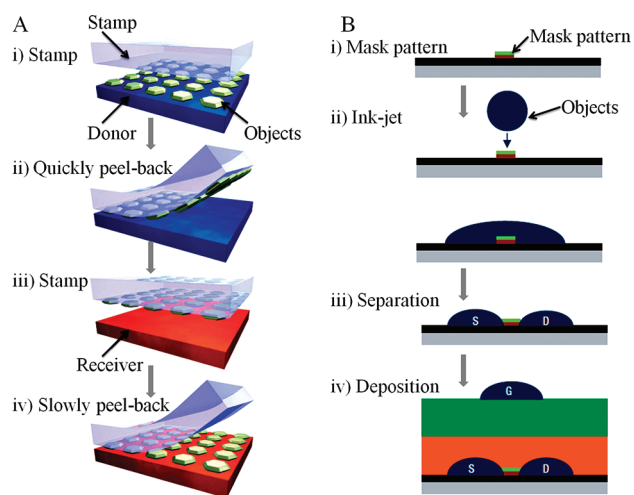


Figure 11. (A) Microcontact printing technique. Adapted with permission from ref 576. Copyright 2006 Macmillan Publishers Limited. The objects can be electrodes,⁵⁷⁷ semiconductors,⁵⁷⁸ insulators,⁵⁷⁹ or even SAM monolayers,³⁹⁴ and the stamp can be reserved as substrates⁵⁷⁹ or separated away from the devices by heat,⁵⁷⁷ solvent,⁵⁸⁰ peel-back' etc. (B) Inkjet printing technique. Adapted with permission from ref 581. Copyright 2004 Macmillan Publishers Limited. The objects can also be electrodes,⁵⁸¹ semiconductors,⁵⁶⁶ or insulators.

transistors are favored as a kind of powerful tool used to reveal the intrinsic properties and structure–property relationships of organic semiconductors. Moreover, single crystal transistors are expected to give higher performances than thin film transistors of the same material.

Organic single crystals can be obtained from physical vapor transport (PVT) systems. A typical PVT system contains two temperature zones, in which organic semiconductors sublimate at the high temperature zone and are crystallized at the low temperature zone. The purity of the semiconductor, the temperature of both the sublimation and crystallization zones, the temperature gradient in the zones, the vacuum level, and even the transport gas are the main parameters that affect molecular packing,⁵⁸² size, morphology,³⁷ and the quality of the crystals (details can be found in a previous review⁵⁸³). There is no doubt that solution-processed techniques such as dip-coating,⁵⁸⁴ drop-casting,²⁴⁴ or solvent-exchanging¹²⁷ have all been explored with a view to growing high quality organic crystals.

Polymers are widely used as the gate insulator for the fabrication of organic single crystal transistors,⁵⁸⁵ such as parylene. It was vaporized at ~ 100 °C, pyrolyzed at ~ 700 °C, and then polymerized in the deposition area by using a tube furnace with three temperature zones.⁵⁸⁶ This processed polymer insulator provided intimate contact between the semiconducting and gate-dielectric layers. Definitely, some small molecules have also been used as gate-dielectric materials in single crystal devices; for example, PQ is used in pentacene-based single crystal transistors, and a high FET performance was obtained.⁵⁸

Organic crystals always exist as nanometer- or micrometer-sized “small” crystals due to the weak van der Waals force between the organic molecules. The small size and fragility of organic crystals present great challenges for the fabrication of their devices not to mention the exploration of their properties. Bottom gate bottom contact mode (Figure 2A) could eliminate the damage from thermal, electron beam, or solvents after the

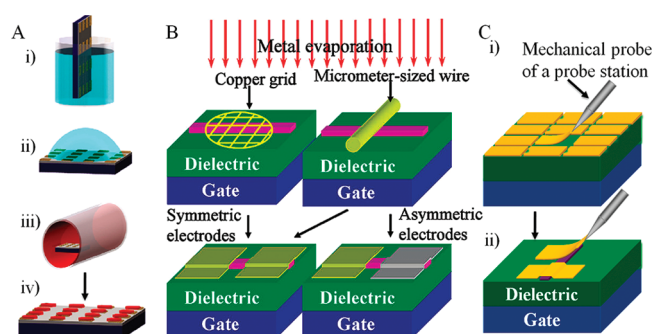


Figure 12. (A) Bottom gate bottom contact configuration with pre-fabricated electrodes through: (i) dip-coating,⁵⁸⁴ (ii) drop-casting, (iii) PVT method³⁹⁴ to prepare (iv) patterned single crystal transistors. Adapted with permission from ref 588. Copyright 2007 Elsevier B.V. (B) Shadow mask technique using a copper grid,⁴¹ micro-/nanometer-sized wire or ribbon (Au-wire,³⁶⁸ polyethylene fiber,⁵⁸⁹ organic micro/nanoribbon,¹⁸⁰ etc.) as mask for electrode deposition. (C) “Gluing Au-films onto crystals”:⁵⁸⁷ (i) peeling off predeposited Au-films by mechanical probe of a probe station, (ii) gluing the Au-films onto crystals directly. Adapted with permission from refs 37 and 590. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA and Copyright 2010 American Chemical Society.

single crystal is prepared (Figure 12A). However, bottom contact mode usually causes poor contact between the crystals and insulators or electrodes. Hence, the top contact configuration (Figure 2B) is worth considering. For example, Au-wires (~ 20 μm)³⁰³ and organic micro/nanoribbons (with diameters from hundreds of nanometers to several micrometers)¹⁰⁹ were explored by Hu et al. Using organic micro-/nanoribbons as shadow-masks, the conducting channel of the devices is decided by the width of the mask ribbon, so that devices based on very small crystals can be fabricated. It is very useful to investigate the transport anisotropy of crystals¹⁸⁰ with the “organic-ribbon mask” technique^{91,180} and even to fabricate asymmetrical devices with a “multiple times mask moving” technique.³⁶⁸ In order to avoid thermal irradiation on the crystals during source/drain electrode deposition, a mechanical approach to glue the Au-films onto the crystals was also developed (Figure 12C).⁵⁸⁷ This made it possible to eliminate the damage of crystals during preparation. But this method is only facile for the laboratory study of crystals because of the limitations of hand manipulation.

6. A GENERAL SURVEY OF π -CONJUGATED SYSTEMS FOR HIGH PERFORMANCE OFETS

Since the first polymer field-effect transistor was reported in the late 1980s, π -conjugated systems have achieved remarkable progress. For example, the mobility of the first polymer OFETs was at around 10^{-5} $\text{cm}^2/(\text{V}\cdot\text{s})$, but to date, many semiconductors exhibit mobilities ≥ 1.0 $\text{cm}^2/(\text{V}\cdot\text{s})$, comparable to or better than that of amorphous silicon. The highest mobility of thin film transistors based on π -conjugated systems has been found to reach as high as 10 $\text{cm}^2/(\text{V}\cdot\text{s})$, and that of single crystals even up to 15 – 40 $\text{cm}^2/(\text{V}\cdot\text{s})$. The molecular structures, energy levels and gaps, mobilities and packing motifs of some representative compounds with a mobility ≥ 1.0 $\text{cm}^2/(\text{V}\cdot\text{s})$ are summarized as p-type and n-type semiconductors in Charts 36 and 37, Tables 2 and 3, respectively. On the basis of the analysis and comparison of different classes of organic compounds, that is, from small molecule semiconductors to polymers, from p-type to n-type,

Table 2. Energy Levels, Mobilities and Packing Motifs of p-Type Organic Semiconductors with Mobilities Higher than $1 \text{ cm}^2/(\text{V}\cdot\text{s})$

	LUMO (eV)	HOMO (eV)	E_g (eV)	packing mode	μ ($\text{cm}^2/(\text{Vs})$)	ref
3a	-2.75	-5.21	2.57	herringbone	2.4 ^b	51, 55
4a	-3.2	-5.0	1.8	herringbone	5 ^a , 40 ^b	53, 56, 58
4b	-2.2	-5.5	3.3	herringbone	1.1 ^a	61
18a	-2.8	-5.4	2.6	herringbone	1.3 ^a , 4.3 ^b	56, 91
18b	-2.9	-5.5	2.6	herringbone	1.28 ^a	90
20b					2.5 ^a	96
25a	-3.15	-5.36	2.21	slipped π -stacking	24.5 ^b	45, S91
25b				slipped π -stacking	12 ^b	118
26d				slipped π -stacking	1.6 ^b	36
26e		-5.7 ^a		slipped π -stacking	1.7 ^b	121
28d	-3.42	-5.11	1.69	2-D π -stacking	1.8 ^a	126, S92
28f	-3.32	-5.19	1.87	1-D π -stacking	2.5 ^a	128
49	-2.2	-5.56	3.36	π -stacking	1.7 ^a	169
50a	-2.0	-5.5	3.5	herringbone	1.76–3.9 ^a (C ₈ H ₁₇ , C ₁₀ H ₂₁ , C ₁₁ H ₂₃ , C ₁₂ H ₂₅ , C ₁₃ H ₂₇)	170, 171
50b	-2.4	-5.6	3.2		2.0 ^a	172
51d	-2.14	-5.6	3.46	herringbone	1.8 ^b	179, 180
52a	-2.44	-5.44	3.0	herringbone	2.9 ^a , 8.3 ^b	183, 184
52b	-2.48	-5.38	2.9		1.9 ^a	183
52c	-2.3~2.4	-5.3~5.4	3.0		8.0 ^a (C ₁₀ H ₂₁)	185
54b	-1.94	-5.31	3.37	slipped π -stacking	1.1 ^b	188
55b		-5.31		2-D π -stacking	1.0 ^a	6, 189
56a				2-D π -stacking	1.5 ^a , 6 ^b	191, 192
60c	-3.18	-5.21	2.03	2-D π -stacking	1.25 ^a	193
64d	-2.51	-5.41	2.90	herringbone	2.0 ^a	206
75b	-2.49	-5.39	2.90	slipped π -stacking	2.66 ^b	224
80a	-2.6	-5.7	3.1		2.1 ^b	231, 589
84a	-2.33	-5.09	2.76	slipped π -stacking	1.2 ^b	240, 593
84g	-2.63	-5.14	2.51	slipped π -stacking	3.6 ^b	243, 244
84j	-2.56	-4.96	2.4	slipped π -stacking	1 ^b	246, 247
84q		-4.61		2-D π -stacking	10 ^b , 3.6 ^a	251
88i–j					1.0 ^a , 1.1 ^a	264
97b	-3.5	-5.2	1.7	π -stacking	1.0 ^b	S94, S95
97k	-4.0	-5.7	1.7	2-D π -stacking	10 ^a	309, S96
97l	-3.9	-5.3	1.4	2-D π -stacking	1.0 ^a	312, S97, S98
101f				slipped π -stacking	1.4 ^a	327
102	-2.6	-5.19	2.59	1-D π -stacking	1.0 ^b	328
106a	-3.03	-5.44	2.41	slipped π -stacking	3.6 ^b	336, 337
145a		-5.1			1 ^a	S11, S99
146g	-3.7	-5.4	1.7		1.2 ^a	S28
148g	-3.57	-5.3	1.73		1.4 ^a	S47, 600

^aThin film transistors. ^bSingle crystal transistors.

from aromatic hydrocarbons, chalcogen-containing heterocyclic semiconductors to nitrogen-containing heterocyclic semiconductors, from halogen-containing semiconductors, cyano-containing semiconductors, carbonyl-containing semiconductors, imides, to fullerene and derivatives, some important conclusions can be drawn. For example:

(1) Among the 53 compounds with mobilities equal or greater than that of amorphous silicon (see Charts 36 and 37), only four candidates (88i,j, 121a, 127b) are oligomers. The others have building blocks of fused rings because fused rings are useful for the extension of the

molecular π systems. This indicates the importance of fused rings for the design and synthesis of organic semiconductors with high mobility.

(2) Although pentacene (4a) showed a high mobility with a herringbone packing motif, among the 53 compounds with mobility equal or greater than that of amorphous silicon (Tables 2 and 3) only nine p-type compounds (3a, 4a, 4b, 18a, 18b, 50a, 51d, 52a, 64d) adopted this packing motif (five compounds of acenes and four of thienoacenes). Since others prefer a π - π stacking, this suggests that (i) for acenes and thienoacenes, a herringbone

Table 3. Energy Levels, Mobilities and Packing Motifs of the n-Type Organic Semiconductors with Mobilities Higher than $1 \text{ cm}^2/(\text{V}\cdot\text{s})$

	LUMO (eV)	HOMO (eV)	E_g (eV)	packing mode	μ ($\text{cm}^2/(\text{Vs})$)	ref
121a	-2.73	-5.63	2.9	2-D π -stacking	1.83 ^a	377
121g	-2.68/2.82	-5.64	2.76		1.2 ^a	376, 383, 417
124a	-4.63	-6.88	2.25	slipped π -stacking	1.6 ^b	395, 601, 602
127b	-3.96	-6.36	2.4		1.7 ^a	405, 406
132g	-3.71	-6.97	3.26	2-D π -stacking	7.5 ^a	423, 603
133c	-3.9	-6.3	2.4	1-D π -stacking	1.7 ^a	417, 433, 434
133e	-3.4	-5.4	2.0		2.1 ^a	438, 604
133p	-4.1	-6.4	2.3	1-D π -stacking	1.44 ^a	417, 442
133q	-4.1	-6.1	2.0	slipped π -stacking	1.4 ^b	444
134r	-4.5	-6.8	2.3	2-D π -stacking	6 ^b (vacuum), 3 ^b (air)	390, 417, 450
141a	-4.5/3.8	-6.2	1.7/2.4		6 ^a	474, 595, 605, 606
160	-4.0	-6.56	2.56		3.4 ^a	568

^aThin film transistors. ^bSingle crystal transistors.

packing motif is an efficient way to achieve a high performance, (ii) generally speaking, π - π stacking is a more efficient way to design and synthesize novel organic semiconductors with high mobility, (iii) appropriate electron-withdrawing groups (or polar groups) indeed facilitate π - π stacking due to the counterbalance with electrostatic repulsion and are favorable for the design and synthesis of new organic semiconductors.

- Among the compounds shown in Table 2, most compounds are chalcogen-containing materials, and only several candidates (97b, 97k, 97l, 101f, 102) are nitrogen-containing. This suggests that the incorporation of the electron-rich element of S is an important pathway to organic semiconductors with high performance.
- Among the 53 compounds with mobility equal or greater than that of amorphous silicon (Tables 2 and 3) only the C₆₀ ones have nonplanar structures. The others possess planar or planar-like conjugated structures, which indicates the generality of planar molecular structures being optimum for organic semiconductors with high mobility.
- Among these 53 compounds, only 7 molecules (4b, 51d, 54b, 60c, 75b, 106a, 146g, and 148g) do not possess C₂ symmetry. This suggests the importance of C₂ symmetry for ordered molecular packing and high FET performance.⁵²³
- As shown in Tables 2 and 3, the HOMO energy levels of most p-type semiconductors are at -5.1 ± 0.3 eV, assuming the electrode materials are gold (Au, ~ -5.1 eV), which matches well with the working function of Au electrodes to facilitate hole injection and transport. As for n-type semiconductors, the LUMO energy levels of the semiconductors should also match with the working function of the electrodes used. Most LUMO energy levels of these n-type semiconductors are about -4.0 eV, and air-stable n-type semiconductors need to have their electron affinity at about 4.0 eV.⁴²

It is obvious that the significant progress of developing π -conjugated systems for OFETs has benefited from the optimization of (i) molecular design (seeking out proper conjugated units as building blocks and the optimization of molecular packing and arrangements) and (ii) device physics such as the optimization of device structure, deposition parameters (vacuum degree, deposition rate, substrate etc.) as well as surface engineering

among others. In order to better understand the fundamental needs for high performance OFETs, molecular design and device physics are addressed briefly in the following sections.

6.1. Molecular Design: Structures and Properties

Mobility is defined as the average drift velocity of charges (holes or electrons) under a unit electric field. High mobility means charges can move efficiently from one molecule to another and hence is closely related with molecular packing motifs. A lamellar packing motif (2D π -stacking) can act as an efficient way for charge transport because it can increase the transfer integrals as much as possible (large overlap) and transport charge carriers through a virtually straight line (the shortest route). For example, it was found that 84q had a mobility exceeding $10 \text{ cm}^2/(\text{V}\cdot\text{s})$ using thermal evaporated TTF-TCNQ films as the source/drain electrode. This was attributed to its close side-by-side and brickwork packing (2D lamellar arrangement) motif. Simultaneously, thin film transistors of 132g exhibited typical n-type performance with mobility as high as $6.2 \text{ cm}^2/(\text{V}\cdot\text{s})$. After prolonged equilibration in argon atmosphere at low humidity, the mobility reached $7.5 \text{ cm}^2/(\text{V}\cdot\text{s})$. It was also assigned to a lamellar packing motif of its molecules with strong π - π intermolecular interactions. Here every molecule interacted with four neighboring molecules so that reticular charge transport was achieved (π - π intermolecular interactions were along the *b* axis with extending interactions along the *a* axis; it is also named brickwork, similar to 28d). Similar rules are easily found for 56a with single crystal mobility of $6 \text{ cm}^2/(\text{V}\cdot\text{s})$, 97k with thin film mobility near $10 \text{ cm}^2/(\text{V}\cdot\text{s})$ and 121a with an electron mobility as high as $1.83 \text{ cm}^2/(\text{V}\cdot\text{s})$, and so forth. Therefore, it is perfectly understandable why the design and synthesis of 2D lamellar molecular π -stacking has been the intense focus of recent research. This has led to different strategies which have been applied to this field such as the introduction of substitutions at the peri-positions of acenes, the introduction of polarity, increasing the C/H ratio or adding heteroatoms to generate hydrogen bonds, introducing halogen-halogen interactions or chalcogen-chalcogen interactions, etc.

It is an efficient strategy to shift the packing motif from herringbone to lamellar packing by introducing substitution on the peri-positions of acenes and heteroacenes. For example, the introduction of aromatic groups at the peri-positions of the acenes

(23a–c and 23e) can result in the appearance of π – π stacking and extend their π -conjugated systems. Certainly, the molecular packing motifs are dependent on the length ratio of the substituents and the acene cores. If the size of the substituents is smaller or larger than half the length of the core, a slipped π -stacking structure might end up being adopted. If the substituent is too small or too large, it might result in herringbone packing. For instance, the substituent sizes of 28b–e were close to half the length of pentacene, and they were all found to adopt lamellar arrangements and 28d (TIPS-PEN) showed a mobility up to $1.8 \text{ cm}^2/(\text{V}\cdot\text{s})$ from its drop-casted films due to its 2D π – π stacking. It should be noted that the strategy of substitution in the side-positions needs to be used very cautiously: (1) the side-substituents do not change the planarity of the backbone (or the core of the materials) but could facilitate charge transport because of its potential to tune the molecular packing. For example, the side-substitutions on the core of the higher acenes or thienoacenes are usually beneficial for charge transport (Charts 5–7 and 13). (2) Side-substitutions on oligomers improperly will make the backbone nonplanar and hamper molecular packing due to steric hindrance. This could result in extremely low mobility (e.g., 36b for oligophenyls, 38l,m for fluorene derivatives, 89d and 120 for oligothiophenes, and head-to-head couplings in polymers).

Compared with the peri-positions of acenes, the end-substituents usually make some contribution to the packing motifs (except for 51b). However, substitutions at the end-positions would efficiently extend the π -conjugated systems because they retain the planarity and linearity of the acene cores. For example, the anthracene derivatives (18a,b) exhibited mobilities as high as $1.3 \text{ cm}^2/(\text{V}\cdot\text{s})$,^{55,89} which was much higher than that of anthracene ($0.02 \text{ cm}^2/(\text{V}\cdot\text{s})$).⁴⁶

The introduction of heteroatoms into π -conjugated systems can also generate π – π stacking because of the decrease in C–H $\cdots\pi$ interactions between molecules. Taking PTA (41) as an example, C–H $\cdots\pi$ intermolecular interactions vanished and π – π stacking (slipped π – π stacking) was observed in the crystals (Figure 8). TTF derivatives (e.g., 84g, 84j, 84q) usually adopt π – π stacking and their mobilities are higher than $0.2 \text{ cm}^2/(\text{V}\cdot\text{s})$. 84q even displayed a mobility as high as $10 \text{ cm}^2/(\text{V}\cdot\text{s})$. It should be noted that much more caution needs to be paid to use this strategy to obtain π – π stacking, because the heteroatoms might introduce other interactions such as chalcogen–chalcogen interactions, hydrogen bond or halogen–halogen interactions simultaneously. For example, 45a, 46a, 47, 51d–e, and 52a adopted typical herringbone packing in their single crystals; however, the related compounds 41, 51a, and 54a adopted a nonconventional herringbone packing with π – π stacking.

Another important method is to form 2D column molecular stacking by increasing the C/H ratio in the molecule. HBC and its derivatives (14) are representative compounds. These disk-shaped structures are efficient for extending the π -systems to form π – π stacking due to the high C/H ratio which reduces the C–H $\cdots\pi$ intermolecular interactions. The high C/H ratio is also one of the reasons that most of fused aromatic compounds (pyrene, perylene, and their derivatives NTCDI, PTCDI, etc.) adopted π – π stacking in their crystals.

Finally, the introduction of polar groups into molecules is also an effective way to obtain the π – π stacking motif as mentioned in section 3.1.1.1, for example, the acene-dione (7b). Because here the polar groups increase the molecular polarity and lead to

a new balance between the electrostatic repulsion and the dipole–dipole attraction so that the lamellar packing is expected irrespective of whether the polar groups are in one or both ends of the molecules, such as the case for the trifluoromethane-based oligomer (121a).

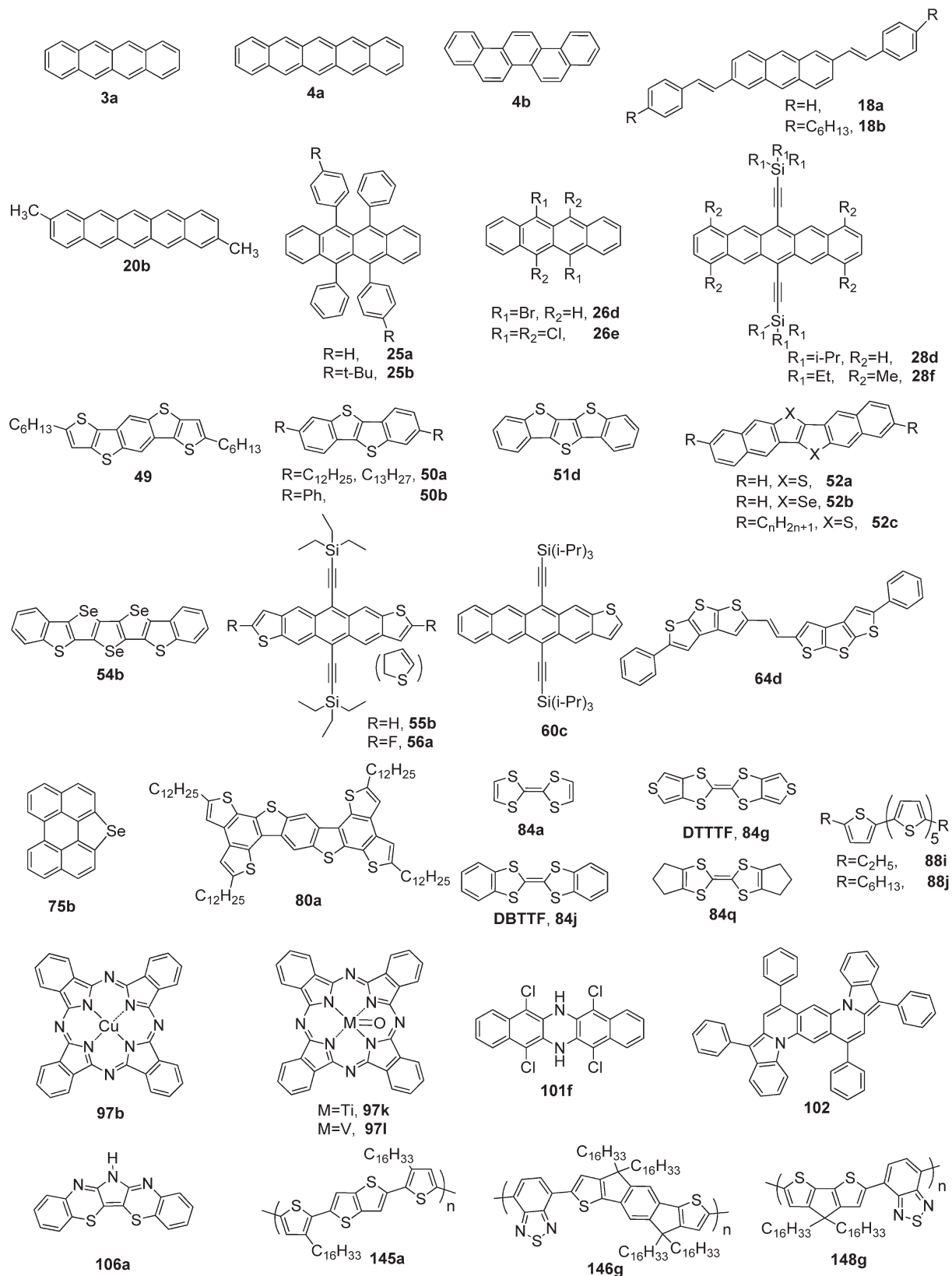
The strategies of design and synthesis of π -conjugated systems with the desired packing motifs are important, for example, 2D lamellar molecular π -stacking. Simultaneously, the tuning of self-assembly processes for controllable packing of molecules into the desired structures is also important for efficient intermolecular charge transport. It has been found that the addition of alkyl side groups or the extension of molecular π -conjugation is working effectively to approach this target. For example, results for 17a–d^{49,86,607} suggest that the tendency of increasing mobilities with the addition of alkyl groups (from 17a to 17b and 17c to 17d) or the extension of molecular π -conjugation (from 17a to 17c and 17b to 17d) is in fact occurring. The derivatives^{87,88} of anthracene substituted by alkylthienyl (17g) showed mobilities nearly 1 order of magnitude higher than that of 17f substituted by thienyl due to the improved self-assembly by the side alkyl chains.

6.2. Device Physics: Materials Orientating Device Optimization

Without doubt in addition to refining the design and synthesis of π -conjugated systems for controlling molecular packing and self-assembly, the purity of the π -conjugated systems and the relevant device physics are also both extremely important for the fabrication of high performance OFETs. It is well-known that impurities in organic semiconductors not only affect the molecular arrangements but also severely trap charge carriers, leading to poor field-effect performance. Therefore, it is important to purify the organic semiconductors to guarantee the required high purity before manufacture. For example, repeated gradient sublimation or using their single crystals as source materials for film deposition can be used.

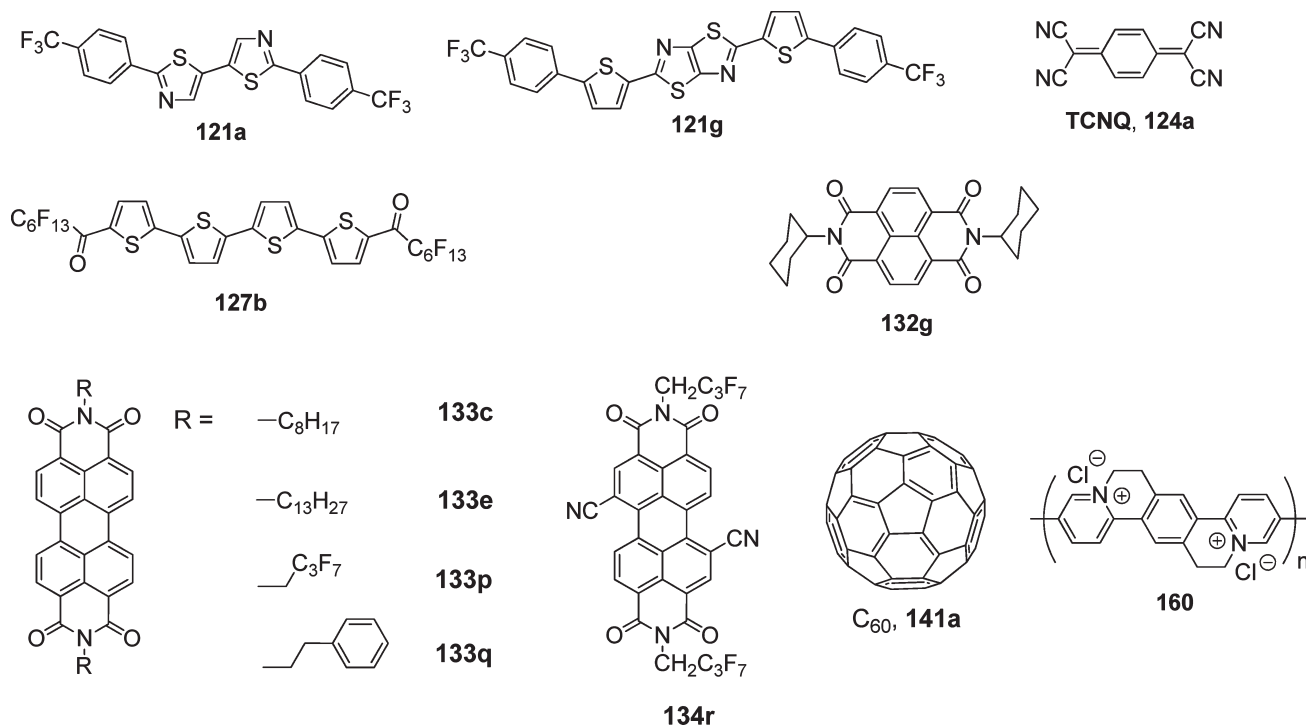
Device physics is a highly interdisciplinary research topic. It is beyond the scope of this review to cover all the studies on this topic; rather, we aim at surveying π -conjugated systems in relation to device optimization, in other words, the effect of the materials on the device optimization. In order to explain it clearly, several examples are now given in order to emphasize the importance of device optimization for obtaining high performance OFETs.

The solid states of π -conjugated systems in OFETs definitely perform an important role in device performances. On one hand, single crystals generally show higher mobility than thin films owing to the highly ordered molecular arrangements, free from grain boundaries and minimized defects in single crystals. For example, single crystals of rubrene showed mobilities as high as $15.4 \text{ cm}^2/(\text{V}\cdot\text{s})$,¹¹⁴ while its thin films showed a highest mobility of only $0.7 \text{ cm}^2/(\text{V}\cdot\text{s})$.^{116,608} Similar results were found for TCNQ (124a). Original tests showed the electron mobility of 124a thin films reached only $10^{-5} \text{ cm}^2/(\text{V}\cdot\text{s})$.⁴¹⁰ However, when microcontact printing techniques were used to pattern 124a crystals for transistor arrays, a higher mobility of about a 10-fold magnification of the thin films was obtained.⁴¹¹ When free-space gate dielectrics (any gas or vacuum) was adopted for 124a single crystal transistors, mobility as high as $1.6 \text{ cm}^2/(\text{V}\cdot\text{s})$ became available.⁴¹² On the other hand, different phases of organic crystals will result in different device properties because of the different molecular packing in the crystals. For example, crystals belonging to the monoclinic α phase of TTF ($1.2 \text{ cm}^2/(\text{V}\cdot\text{s})$)²⁴⁰

Chart 36. p-Type Organic Semiconductors with Mobilities Higher than $1 \text{ cm}^2/(\text{Vs})$ 

exhibited higher mobility than those belonging to the triclinic β phase TTF ($0.23 \text{ cm}^2/(\text{V}\cdot\text{s})$), due to the stronger $\pi-\pi$

stacking along the b axis in phase α . And a similar case was found for crystals of CuPc (**97b**)⁵⁸² and BPEA (**23a**).⁶⁰⁹ These

Chart 37. n-Type Organic Semiconductors with Mobilities Higher than $1 \text{ cm}^2/(\text{Vs})$ 

results emphasize the importance of the crystal phase for device fabrication.

Blending semiconductors of small molecules or polymers has advanced rapidly in recent years. This strategy could combine the high performance of small molecules and ideal film forming ability or solution-processability of polymers thus providing a prospective pathway for using small molecular semiconductors in flexible electronics. For example, thin films of rubrene (**25a**) usually showed rather low mobility because of poor film-forming ability; however, blends of rubrene and polymer made it possible to form continuous crystalline films with mobilities as high as $0.7 \text{ cm}^2/(\text{V}\cdot\text{s})$.¹¹⁶ Moreover, blending systems can significantly simplify the technological process. They are particularly intriguing for the blending of p- and n-type components together for the generation of ambipolar systems, which are especially useful for the fabrication of ambipolar transistors and complementary circuits.⁶¹⁰ Zhu et al.⁶¹¹ found organic donors could facilitate charge transport in n-type organic semiconductors because they increased the order of molecular stacking and the crystallinity of the organic films; that is, they decreased the grain boundaries after blending. In addition, blending systems can improve the stability of the organic semiconductors, especially for the insulating polymer-containing systems. For example, when P3HT was embedded in amorphous polystyrene (PS), it easily formed 1D nanowires,⁶¹² and the blends exhibited transistor behavior with high environmental stability even with a content of P3HT as low as 3 wt %. Finally, it is highly attractive to control the phase separation in blending systems to obtain crystalline films for high performance devices; for example, when TIPS-PEN (**28d**) or **56a** was blended with poly(triarylamine) (PTAA),⁶¹³ the blends showed mobilities as high as 1.1 or $2.4 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively, higher than the single component values.

Charge transport in OFETs is critically dependent on the dielectric layer including the dielectric constant, thickness,

polarity, compactness, etc.; for example, high dielectric constants (high k)⁴³ make it possible to scale down the device dimensions, lower the driving voltage, and increase the circuit integrated degree. On the other hand, the polarity of the dielectric layer could affect the density of states (DOS) in the organic semiconductor and consequently dominate the mobility of the devices.^{553,614} Moreover, because the conduction channel in OFETs exists exactly at the interface between the organic semiconductor and the gate dielectrics, it follows that the contact of the interface plays a key role in the OFET performance. Among the candidates for gate insulators, polymer insulators are highly promising for use in flexible electronics in order to make intimate contact between the dielectric layer and the organic semiconductor. The modification of gate insulators for the optimization of insulator/semiconductor interfaces is important for achieving high device performance, such as SiO_2 modification by OTS or other monolayers, because the compact monolayer not only lowers the leakage current but also improves the wettability of the gate insulator to increase the ordering or crystallization of the organic semiconducting layers. For example, octadecylphosphonic acid (ODPA) has been used to induce the growth of crystalline films of 6,13-pentacenequinone (**7a**, PQ), on which crystalline and continuous rubrene films were obtained.⁶⁰⁸ Subsequently, the devices obtained displayed mobilities as high as $0.35 \text{ cm}^2/(\text{V}\cdot\text{s})$. Furthermore, OFETs⁴⁶⁹ based on C₆₀ (**141a**) thin films provided mobilities of $0.08 \text{ cm}^2/(\text{V}\cdot\text{s})$. When a pentacene monolayer⁴⁷³ was introduced into devices to act as a buffer layer to improve the wettability of the substrates, the modified **141a** devices displayed electron mobilities in the range $2.0\text{--}4.9 \text{ cm}^2/(\text{V}\cdot\text{s})$, and in addition exhibited significant ambipolar behavior. The mobility of **141a** reached $6 \text{ cm}^2/(\text{V}\cdot\text{s})$ ⁴⁷⁴ by using polymer as a dielectric layer and $5.3 \text{ cm}^2/(\text{V}\cdot\text{s})$ ⁴⁷⁷ by using crystalline self-assembly OTMS monolayers and treated

SiO₂ as the gate insulator. A SAM monolayer⁶¹⁵ itself was used as the dielectric layer with smooth surface and low surface energy, so that SAM devices reduced the thickness of the dielectric layer and lowered their driving voltage.

It was also found that annealing the semiconducting layer is very important to make OFETs with high performance because the molecular packing order in films and the contact between the organic semiconductor and the gate insulator are both improved after annealing.²⁶ For example, **133e** showed mobility at 0.58 cm²/(V·s) without annealing, but the mobility approached 2.1 cm²/(V·s) after annealing at 140 °C.⁴⁵⁷ Similarly, the energy level alignment between organic semiconductors and source/drain electrodes is crucial for getting high performance devices because the energy barriers between them actually determine the carrier injection and transport in semiconductors. As shown in Tables 2 and 3, the HOMO energy levels of most p-type semiconductors lie around -5.1 ± 0.3 eV, which matches well with electrode materials having high working functions such as Au and Pt (~ -5.1 eV) which in turn facilitates hole injection and transport. Most LUMO energy levels of n-type semiconductors are close to -4.0 eV, which in turn matches well with electrodes with low work function such as Ag and Ca/Al. It is understandable why some typical p-type semiconductors (e.g., rubrene) exhibit ambipolar characteristics when using Ag or Ca electrodes.^{117,290} Moreover, except for the energy alignment between organic semiconductors and electrode materials, the quality of the interface between the organic semiconductors and electrode materials is also highly critical for the fabrication of high performance OFETs. For example, the HOMO energy level of BNT⁴⁴ is about -5.73 eV, which matched better with Au (-5.1 eV) than the TTF-TCNQ complex (-4.64 to -4.78 eV), but the transistors using TTF-TCNQ as the source and drain electrodes showed mobilities 4 orders of magnitude higher than Au electrodes. This was attributed to the better contact between the organic–organic interfaces than for the organic–inorganic contacts. This conclusion was further supported by results for **84q**, where thermally evaporated TTF-TCNQ films were used as the source/drain electrodes and mobility exceeded 10 cm²/(Vs).²⁵⁰

Finally, other factors such as the device configuration, the thickness of the semiconducting layer, the channel length and width, etc. also play important roles in the optimization of OFETs. Objectively speaking, the experimental testing conditions such as temperature, humidity, and vacuum degree, etc. also participate in the performance evaluation of the devices. Without a doubt, in order to obtain high performance devices, systematic engineering involving device physics is absolutely necessary; this includes the delicate control of the organic semiconductor layer as well as the interfacial engineering of the organic semiconductor/insulator and organic semiconductor/electrodes.

7. CONCLUDING REMARKS AND OUTLOOK

In this article, 160 kinds of π -conjugated systems (709 compounds) were carefully reviewed; these included 438 p-type small molecules, 205 n-type small molecules, and 66 polymer semiconductors. Of these 53 compounds with mobilities higher than 1 cm²/(V·s) are highlighted. On the basis of the systematic and statistical analysis of these π -conjugated systems, some important clues regarding molecular design and device physics are given (in section 6). For example, it is found that it is possible to control the molecular weight of donor–acceptor copolymers

as an efficient way to achieve high mobility (3.3 cm²/(V·s))⁶¹⁶ because with increasing molecular weight the crystallinity of the polymers is also increased. It is hoped that this review will make a stimulating contribution to a better understanding of the structure–property relationships of π -conjugated systems, to clarify the ideal requirements for new materials, and finally how to optimize devices based on these π -conjugated systems to achieve OFETs with high performance.

Regardless of the rapid progress of π -conjugated systems and their application in OFETs, however, it is worth noting that there remain challenges for the application of OFETs in organic electronics because (i) the mobilities of π -conjugated systems still lags behind their inorganic counterparts such as silicon, especially for solution-processed, printed compounds such as polymers. Hence, how to design π -conjugated systems with even high mobility remains a hard task, although in principle π -conjugated systems constitute the possibility (e.g., graphene with super high mobility); (ii) the charge transport mechanism of π -conjugated systems in OFETs is still undefined and the relationships among chemical structure, molecular packing, intermolecular interactions, and properties remain unclear. This not only hampers scientists designing novel π -conjugated systems for high performance but also makes it more difficult to predict their properties in turn. Simultaneously, dielectric materials and electrode materials also take on important roles in field-effect transistors, and hence the matching of these materials and interface engineering need to be taken into account for the industrial large-scale application of π -conjugated systems in organic electronics in the near future. In conclusion, it is hoped that this “Material Odyssey of Organic Electronics” helps to inspire the next stages in this exciting field of research.

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